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**U.S. ARMY SOLDIER AND BIOLOGICAL CHEMICAL COMMAND**

**ECBC-TR-323**

**INFRARED SPECTROSCOPIC OBSERVATIONS  
ON THE FATE  
OF ORGANOPHOSPHORUS COMPOUNDS EXPOSED  
TO ATMOSPHERIC MOISTURE**

**PART I. G-AGENTS AND RELATED COMPOUNDS**

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**JULY 2003**

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## **PREFACE**

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This work is based on infrared spectroscopic data obtained from 1979 through 1992.

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INFRARED SPECTROSCOPIC OBSERVATIONS ON THE FATE OF ORGANOPHOSPHORUS  
COMPOUNDS EXPOSED TO ATMOSPHERIC MOISTURE  
PART I. G-AGENTS AND RELATED COMPOUNDS

**1. INTRODUCTION**

Many infrared spectra have been collected over the years pertaining to chemical agents and related compounds (precursors and impurities). After initial spectra were obtained for many of these compounds the original pure material was allowed to remain between salt windows and repeated scans made with time as the material sat (in a fume hood) exposed to the atmospheric moisture. This report will present and discuss the spectra obtained for many organophosphorus compounds as they sat exposed to atmospheric moisture. These spectra should be of interest to the Chemical Weapons (CW) treaty verification program as many of the studied compounds comprise Schedules 1, 2, and 3 materials of the Chemical Weapons Convention. This data should be of value as part of the verification regime that includes on-site inspection of declared chemical warfare related facilities. Infrared analysis of bulk (near) hazardous material is rapid and efficient and offers minimal sample preparation.

**2. EXPERIMENTATION**

**2.1 Instrumentation**

All the spectra included in this report were determined on either a Nicolet Model 10 DX (Nicolet Analytical Instruments, Madison, WI) or on a Perkin-Elmer Model 1750 (Perkin-Elmer Corporation, Norwalk, CT) Fourier Transform spectrometer. The spectra were saved on individual magnetic floppy disks that were resident to the particular instrument used. The spectra were also transferred to a Zenith PC via a Sprouse Scientific Micro-Trace program (Sprouse Scientific Systems, Incorporated, Paoli, PA) for inclusion into a central search system. Hard copies of the spectra were plotted on a Hewlett-Packard Model 7475A plotter (Hewlett-Packard, Palo, Alto, CA). Some Spectra were also plotted utilizing Nicolet Omnic® FT-IR software and Epson *Stylus*® color printer (Epson America, Inc.). The instruments were purged with the boil off from a liquid nitrogen cryogenic container. The sample compartments of the instruments were placed inside fume hoods as a safety precaution.

## 2.2 Sample Handling

Liquid samples were determined as capillary films (neat) between 25 mm diameter X 4 mm thick KBr or CsI discs at a resolution of  $2\text{ cm}^{-1}$ . After an initial spectrum was obtained, the sample film/salt window sandwich was allowed to sit in the hood air for a period of time, then returned to the sample compartment of the instrument and a spectrum determined. The sample film was returned to the hood air and allowed to sit until the sample was completely hydrolyzed as evidenced by no further changes occurring in the infrared spectrum.

Solid samples were run as either KBr pellets or directly as solids between KBr or CsI windows (disc). Potassium bromide pellets were prepared using infrared grade KBr (Harshaw Chemical Company, Cleveland, OH). The sample KBr matrix was ground in a stainless steel vial with a Wig-L-Bug amalgamator (Crescent Dental Manufacturing Company, Chicago, IL). Some of the solid samples were determined directly (no KBr matrix) by placing a small amount of solid (1 mg or less) between two polished salt discs. The solid was ground by moving the salt discs across one another with a back and forth motion, alternating with a figure-eight motion. This grinding lasted about 20 seconds. An IR spectrum was then determined to see if the grinding was sufficient to produce an acceptable spectrum, one essentially free of distorted band shapes. The spectra thus produced by this second method were smoothed, flattened and ordinate expanded as needed.

Vapor phase spectra were determined at a resolution of  $1\text{ cm}^{-1}$ , in a 10 cm glass body gas cell having two stopcocks, one of which was fitted with a rubber sleeve septum, for injection of liquid samples. The cell was equipped with demountable KBr windows. A Teflon body gas cell equipped with CdTe windows was also used to determine vapor phase spectra. Initial vapor phase spectra were determined in an evacuated cell first, then air was admitted by momentarily opening one stopcock. Scans were then repeated, over a period of time, for the vapor samples now containing air. The procedure followed for vapor sample was similar to that used for liquid samples as discussed above.

### 2.3 List of Compounds (The CAS number is given in the [ ])

All the following compounds were used as received, with no further purification.

<b>GA Tabun</b> , ethyl N,N-dimethylphosphoramidocyanidate	[77-81-6]	<b>Figs. 21, 22</b>
<b>GA PYRO</b> , bis(ethyl N,N-dimethylphosphoramidic) anhydride, <i>sym</i> -Bis(dimethylamido)-diethyl pyrophosphate		<b>Figs. 23, 24</b>
<b>GB, Sarin</b> , isopropyl methylphosphonofluoridate	[107-44-8]	<b>Figs. 1, 2</b>
<b>GD, Soman</b> , pinacolyl methylphosphonofluoridate [96-64-0], stabilized with DICDI (1,3-diisopropylcarbodiimide)	[693-13-0]	<b>Figs. 3, 4</b>
<b>GF</b> , cyclohexyl methylphosphonofluoridate	[329-99-7]	<b>Figs. 5, 6-9</b>
<b>EA 1356</b> , 2-methylcyclohexyl methylphosphonofluoridate	[85473-32-1]	<b>Figs. 10, 11</b>
<b>EA 1232</b> , methyl methylphosphonofluoridate	[353-88-8]	<b>Figs. 12, 13</b>
<i>n</i> -Butyl isopropylphosphonofluoridate		<b>Figs. 14, 15</b>
Ethyl vinylphosphonofluoridate		<b>Figs. 16, 17A-B</b>
Trimethylsilyl N,N-dimethylphosphoramidofluoridate		<b>Fig. 25A-B</b>
Trimethylsilyl methylphosphonocyanidate		<b>Figs. 18, 19</b>
Ethyl dichlorophosphate (ethyl phosphorodichloridate)	[1498-51-7]	<b>Figs. 72, 73</b>
<b>Fluoro Acid</b> , methylphosphonofluoridic acid	[1511-67-7]	<b>Figs. 53, 55</b>
<b>Sodium salt of GA acid</b> ; ethyl N,N-dimethylamidophosphoric acid, sodium salt		<b>Fig. 79</b>
<b>IMPA, GB Acid</b> , isopropyl methylphosphonic acid	[5514-35-2]	<b>Fig. 46</b>
<b>PMPA, GD Acid</b> , pinacolyl methylphosphonic acid	[616-52-4]	<b>Fig. 60</b>
<b>CMPA, GF Acid</b> , cyclohexyl methylphosphonic acid	[1932-60-1]	<b>Fig. 59</b>
<b>EA 1356 Acid</b> , 2-methylcyclohexyl methylphosphonic acid		<b>Fig. 63</b>
<b>MPA</b> , methylphosphonic acid	[993-13-5]	<b>Figs. 20 &amp; 54 (wet); 47, 48</b>
Methylphosphonic anhydride		<b>Figs. 49, 50</b>

<b>NAIMP</b> , sodium isopropyl methylphosphonate (isopropyl methylphosphonic acid, sodium salt)		<b>Fig. 66</b>
<b>NA<sub>2</sub>MP</b> , disodium methylphosphonate (methylphosphonic acid, disodium salt)		<b>Fig. 65</b>
<b>NAMPA</b> , methylphosphonic acid monosodium salt		<b>Fig. 64</b>
<b>NA<sub>2</sub>PYRO</b> , disodium dimethylpyrophosphonate		<b>Fig. 67</b>
<b>DMMP</b> , dimethyl methylphosphonate	[756-79-6]	<b>Figs. 43, 44</b>
<b>DIMP</b> , diisopropyl methylphosphonate	[1445-75-6]	<b>Figs. 56, 57</b>
<b>DPMP</b> , dipinacolyl methylphosphonate	[7040-58-6]	<b>Fig 61</b>
<b>N,N</b> -dimethylphosphoramidic dichloride	[1899-02-1]	<b>Figs. 70, 71</b>
<b>TH</b> , Phosphorus trichloride	[7719-12-2]	<b>Figs. 32, 33</b>
Pinacolyl alcohol (3-dimethyl-2-butanol; 1,2,2-trimethyl-1-propanol)	[464-07-3]	<b>Fig. 62</b>
Pinacolone, ( <i>tert</i> -butyl methyl ketone; 3,3-dimethyl-2-butanone)	[75-97-8]	<b>Fig. 45</b>
<b>SW</b> , methylphosphonous dichloride	[676-83-5]	<b>Figs. 26, 27</b>
<b>DC, Dichlor</b> , methylphosphonic dichloride	[676-97-1]	<b>Fig. 29</b>
Methylphosphonic chlorofluoride		<b>Figs. 30, 31</b>
<b>DF, Difluor</b> , methylphosphonic difluoride	[676-99-3]	<b>Figs. 51, 52A-E</b>
Dimethyl phosphite	[868-85-9]	<b>Figs. 34, 35</b>
<b>TMP</b> , trimethyl phosphite	[121-45-9]	<b>Figs. 36, 37</b>
Diisopropyl phosphite	[1809-20-7]	<b>Figs. 38, 39</b>
Triisopropyl phosphite	[116-17-6]	<b>Figs. 40, 41; 42A-F</b>
<b>THO</b> , phosphorus oxychloride (phospheryl chloride)	[10025-87-3]	<b>Fig. 69</b>
<b>TEPO</b> , triethyl phosphate	[78-40-0]	<b>Figs. 74, 75</b>
Dimethylamine hydrochloride	[506-59-2]	<b>Fig. 68</b>
Hydroxylamine hydrochloride	[5470-11-1]	<b>Fig. 76</b>
Phosphoric acid	[7664-38-2]	<b>Fig. 77</b>

2-Propanol (isopropyl alcohol)	[67-63-0]	Fig. 58
Ethyl alcohol	[64-17-5]	Fig. 78
Methylphosphonocyanidic fluoride		Figs. 80A-B, 81
Phenyl methylphosphonofluoridate		Figs. 82, 83, 84
Diethyl cyanophosphonate	[2537-48-6]	Figs. 85, 86
<i>t</i> -Butylphosphonic difluoride		Fig. 87
<i>t</i> -Butylphosphonic acid		Fig. 88
Isopropyl <i>t</i> -butylphosphonofluoridate		Fig. 89
Isobutyl <i>t</i> -butylphosphonofluoridate		Fig. 90
Isobutyl hydrogenmethylphosphinate		Figs. 91, 92A-D

## 2.4 List of Abbreviations

### Band Intensities

w weak  
m medium  
s strong  
v very  
sh shoulder

### Vibrations

v stretching  
as asymmetric  
sy symmetric  
 $\delta$  deformation  
 $\omega$  wagging  
 $\tau$  twisting  
 $\beta$  in-plane deformation  
 $\gamma$  out-of-plane deformation

### 3. RESULTS AND DISCUSSION

#### 3.1 G-Type Agents

##### 3.1.1 Isopropyl Methylphosphonofluoridate (GB, Sarin) $\text{CH}_3\text{P}=\text{O}(\text{F})[\text{O}-\text{CH}(\text{CH}_3)_2]$

The infrared spectrum of **GB (Sarin)** is given in *Figure 1*. The infrared bands may be assigned as follows: 2986  $\text{cm}^{-1}$  m and 2935  $\text{cm}^{-1}$  w (aliphatic CH stretching), 1469 and 1458  $\text{cm}^{-1}$  vw ( $\delta$   $\text{CH}_3$ ), 1420  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ), 1389 and 1379  $\text{cm}^{-1}$  m [ $\delta_{\text{sy}}$   $\text{CH}_3$  (isopropyl)], 1321  $\text{cm}^{-1}$  ms ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ), 1278  $\text{cm}^{-1}$  s ( $\nu$  P=O), 1180, 1145 and 1106  $\text{cm}^{-1}$  all weak (characteristic of P-O-isopropyl), 1015  $\text{cm}^{-1}$  s ( $\nu$  P-O-C), 924 and 907  $\text{cm}^{-1}$  m ( $\text{CH}_3$  rock of P- $\text{CH}_3$  and isopropyl), 838  $\text{cm}^{-1}$  ms ( $\nu$  P-F), 778  $\text{cm}^{-1}$  w (POC), 723  $\text{cm}^{-1}$  w ( $\nu$  P-C).

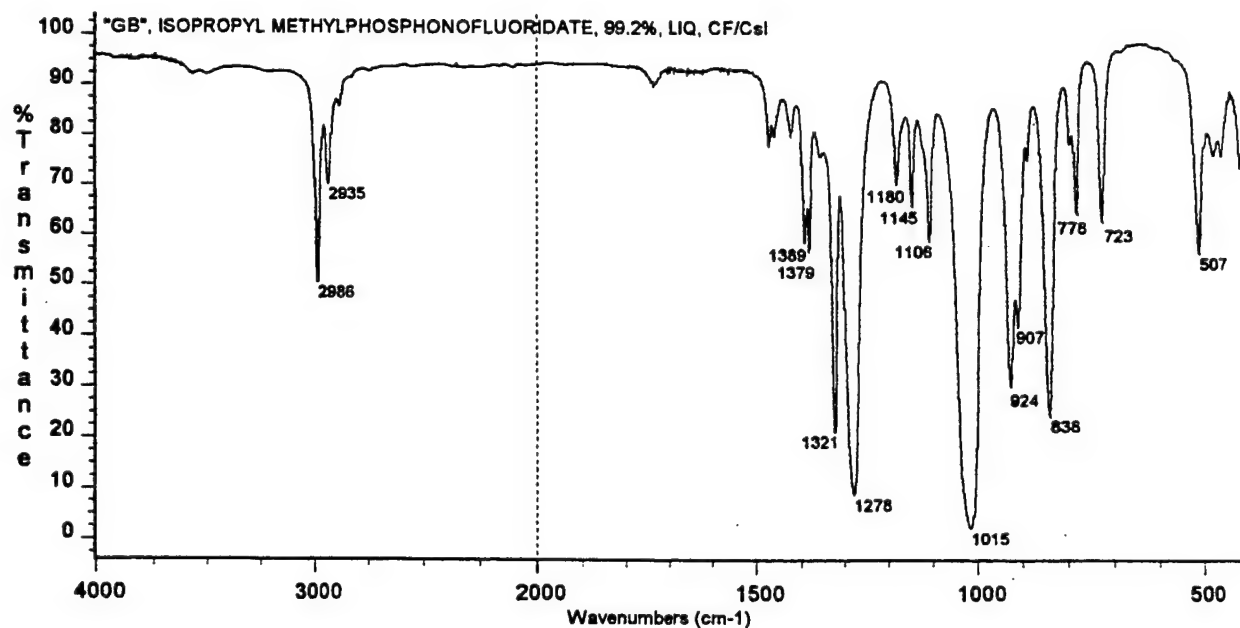
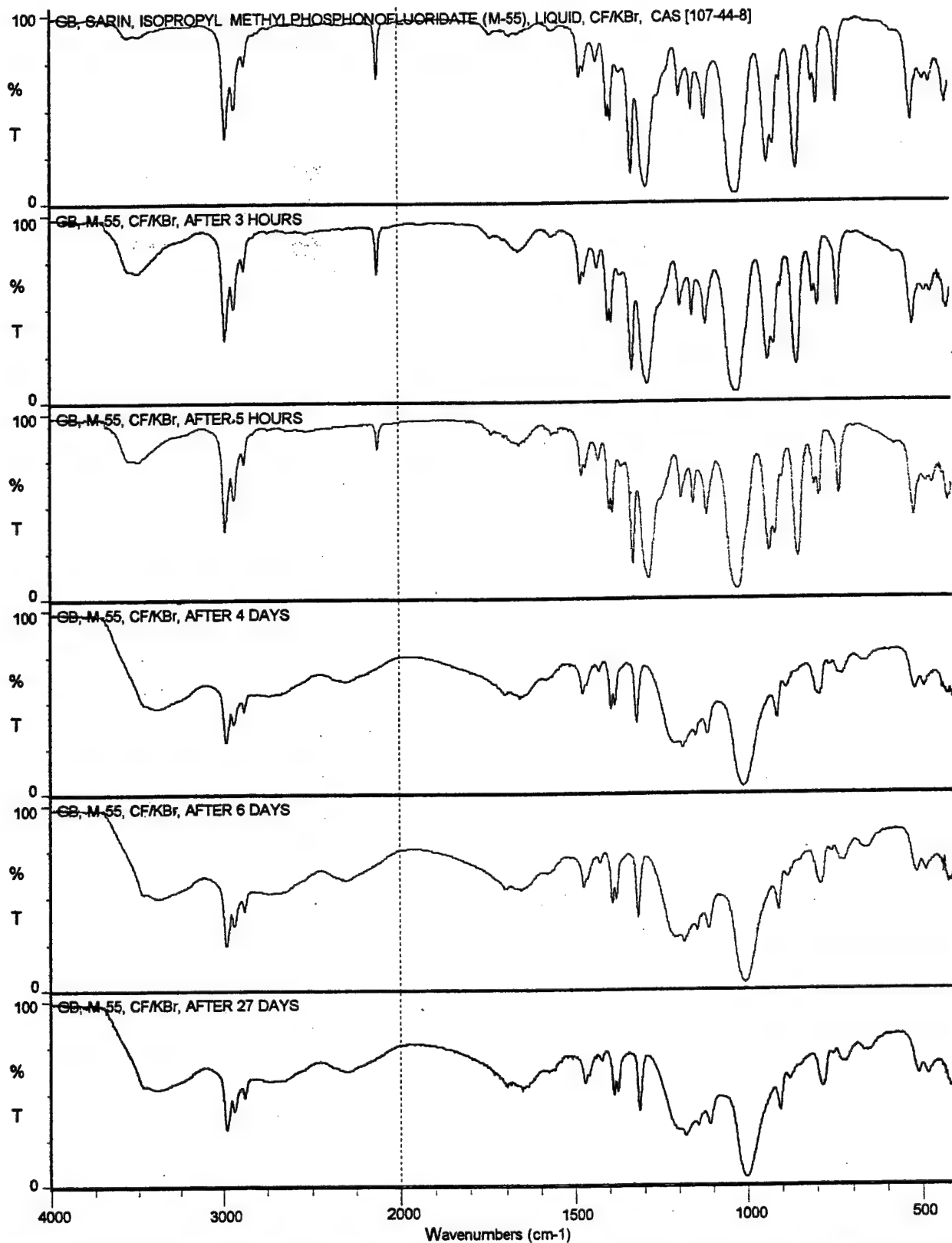


Figure 1 GB, SARIN, ISOPROPYL METHYLPHOSPHONOFUORIDATE, 99.2%, LIQUID, CF/CsI

The effect of atmospheric moisture on a liquid sample of **GB** while between KBr windows is represented by *Figure 2*. The top spectrum in the figure shows **GB** (stabilized with CDI, a carbodiimide) at time zero. Succeeding spectra show the effect of moisture, with time, on the **GB** sample. After some 4 days the resulting spectrum is that of **GB ACID**, isopropyl methylphosphonic acid (isopropyl hydrogen methylphosphonate),  $\text{CH}_3\text{P}=\text{O}(\text{OH})[\text{O}-\text{CH}(\text{CH}_3)_2]$ .

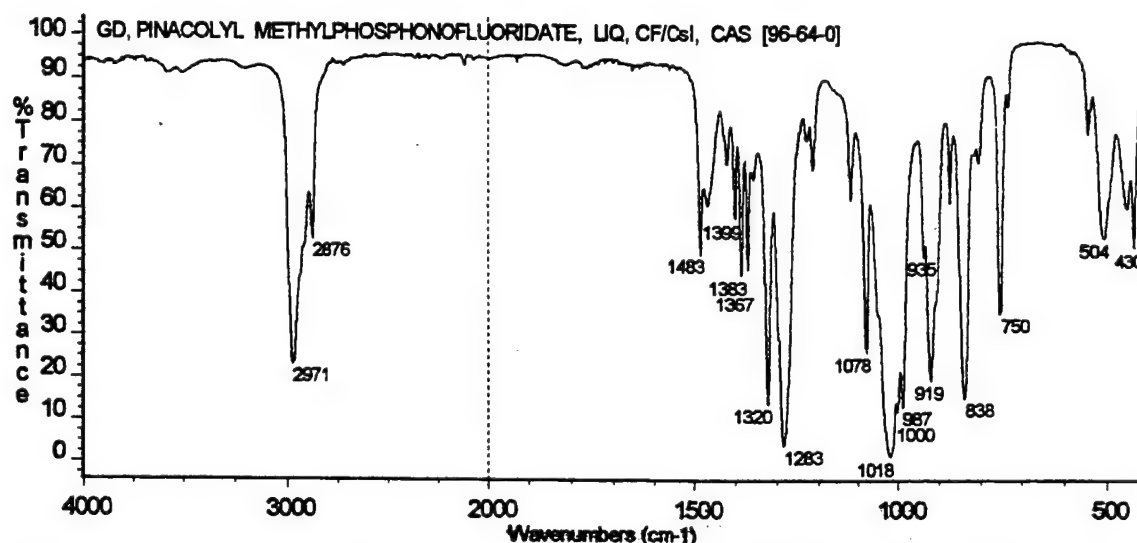




**Figure 2 MUNITION ROUND GB (WITH A CARBODIIMIDE ), LIQUID, CF/KBr, EXPOSED TO ATMOSPHERIC MOISTURE**

### 3.1.2 Pinacolyl Methylphosphonofluoridate (GD, Soman) $\text{CH}_3\text{P}=\text{O}(\text{F})[\text{O}-\text{CH}(\text{CH}_3)\text{C}(\text{CH}_3)_3]$

The infrared spectrum of GD (Soman) is given in *Figure 3*. The infrared bands may be assigned as follows:  $2971\text{ cm}^{-1}$  ms and  $2876\text{ cm}^{-1}$  m (aliphatic CH stretching),  $1483\text{ cm}^{-1}$  m and  $1464\text{ cm}^{-1}$  w ( $\delta$   $\text{CH}_3$ ),  $1418\text{ cm}^{-1}$  vw ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ),  $1399\text{ cm}^{-1}$  w,  $1383\text{ cm}^{-1}$  m and  $1367\text{ cm}^{-1}$  m ( $\delta_{\text{sy}}$  C- $\text{CH}_3$ ),  $1320\text{ cm}^{-1}$  ms ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ),  $1283\text{ cm}^{-1}$  s ( $\nu$  P=O),  $1226\text{ cm}^{-1}$  vw,  $1211\text{ cm}^{-1}$  w,  $1117\text{ cm}^{-1}$  w and  $1078\text{ cm}^{-1}$  m (pinacolyl moiety),  $1018\text{ cm}^{-1}$  s ( $\nu$  P-O-C),  $987\text{ cm}^{-1}$  m ( $\nu$  C-C of pinacolyl moiety),  $935\text{ cm}^{-1}$  w,  $919\text{ cm}^{-1}$  m and  $871\text{ cm}^{-1}$  w ( $\text{CH}_3$  rock of P- $\text{CH}_3$  and C- $\text{CH}_3$ ),  $838\text{ cm}^{-1}$  ms ( $\nu$  P-F),  $750\text{ cm}^{-1}$  m ( $\nu$  P-C),  $504\text{ cm}^{-1}$  m ( $\delta$  P=O ?).



**Figure 3 GD, PINACOLYL METHYLPHOSPHONOFUORIDATE, 99%, LIQUID, CF/CsI**

The effect of atmospheric moisture on a thin film of GD liquid between KBr windows is given in *Figure 4*. The top spectrum is that for a sample of GD stabilized with DICDI (diisopropyl carbodiimide). After 2.5 hours the band due to DICDI at  $2115\text{ cm}^{-1}$  is decreasing in intensity as the compound begins to pick up moisture. After 72 hours the spectrum resembles that of a phosphonic acid, namely, pinacolyl methylphosphonic acid (pinacolyl hydrogen methylphosphonate). Acid bands are evident in the spectrum at ca.  $2700$ ,  $2298$ ,  $1670$  and  $1208\text{ cm}^{-1}$ . The P-O-C band (pinacolyl moiety) occurs at ca.  $1016\text{ cm}^{-1}$ .

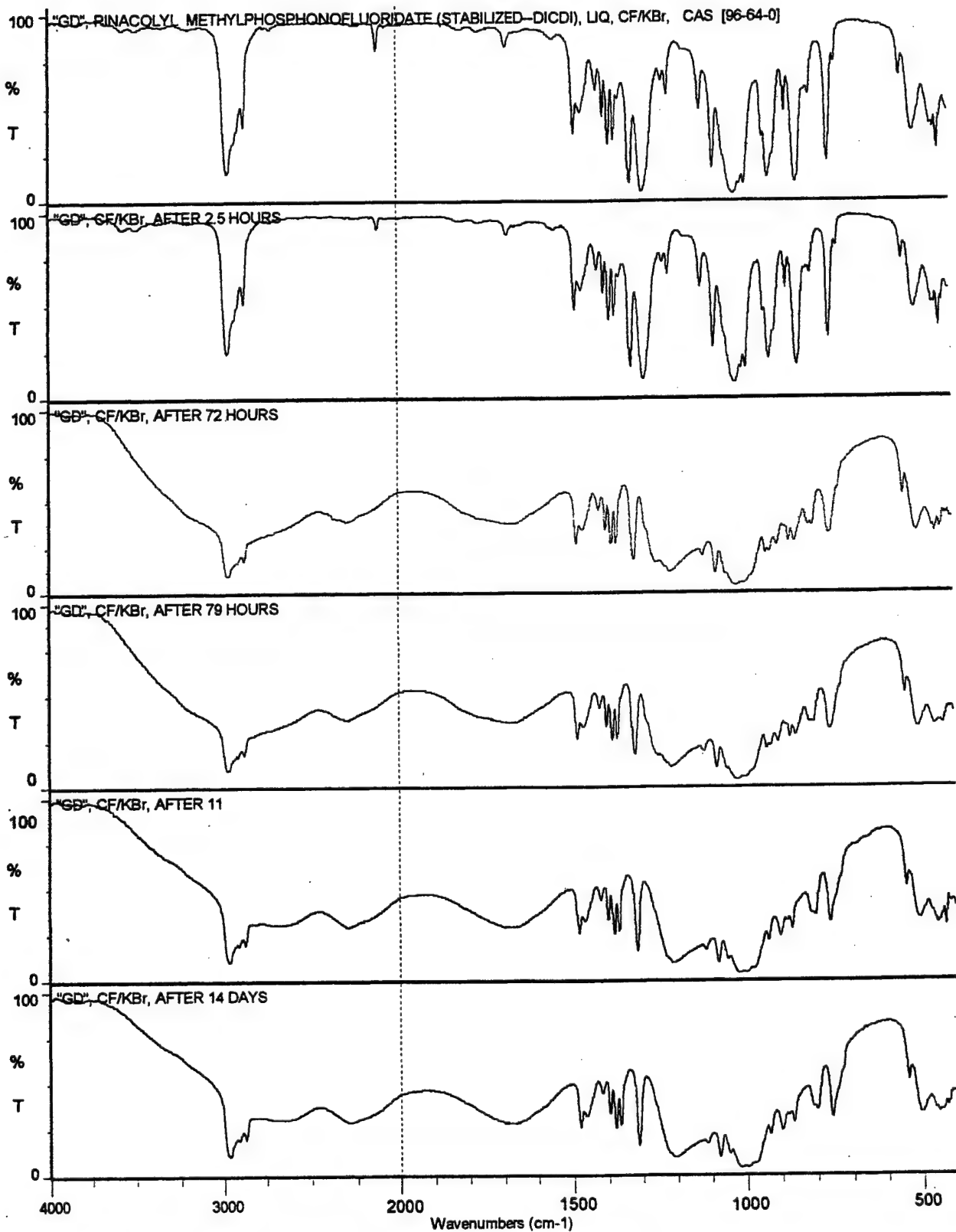
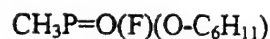


Figure 4 GD, LIQUID, CF/KBr, EXPOSED TO ATMOSPHERIC MOISTURE

### 3.1.3 Cyclohexyl Methylphosphonofluoridate (GF)



The infrared spectrum for GF is given in *Figure 5*. The infrared bands may be assigned as follows:  $2999\text{ cm}^{-1}$  vw,  $2940\text{ cm}^{-1}$  ms,  $2862\text{ cm}^{-1}$  m (aliphatic  $\nu$  CH),  $1453\text{ cm}^{-1}$  w ( $\delta$  CH ring),  $1418\text{ cm}^{-1}$  vw ( $\delta_{\text{as}}$  P-CH<sub>3</sub>),  $1321\text{ cm}^{-1}$  ms ( $\delta_{\text{sy}}$  P-CH<sub>3</sub>),  $1281\text{ cm}^{-1}$  s ( $\nu$  P=O),  $1039\text{ cm}^{-1}$  sh and  $1017\text{ cm}^{-1}$  s ( $\nu$  P-O-C),  $907\text{ cm}^{-1}$  m (P-CH<sub>3</sub> rock),  $753\text{ cm}^{-1}$  m ( $\nu$  P-C),  $503\text{ cm}^{-1}$  w ( $\delta$  P=O ?).

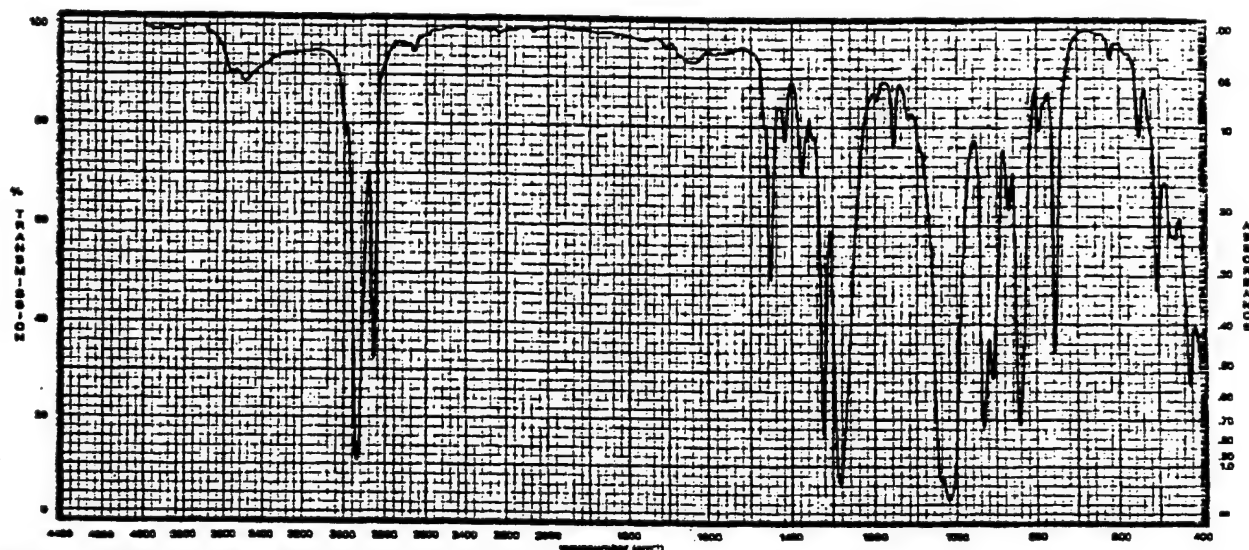


Figure 5 GF, CYCLOHEXYL METHYLPHOSPHONOFUORIDATE, LIQUID, CF/KBr

The effect of atmospheric moisture of the infrared spectrum of GF is given in *Figures 6 through 9*. After 22 hours, the infrared spectrum (*Figure 7*) shows the presence of bands indicative of a P-acid, namely ca  $2800$ , ca  $2300$  and ca  $1700\text{ cm}^{-1}$  (POH), ca  $1200\text{ cm}^{-1}$  ( $\nu$  P=O), ca  $1020\text{ cm}^{-1}$  ( $\nu$  P-OH). A band is also present near  $1250\text{ cm}^{-1}$  which may be due to the P=O stretch of a pyro compound namely, dicyclohexyl dimethylpyrophosphate,  $(\text{C}_6\text{H}_{11}\text{O})\text{CH}_3\text{P}(=\text{O})-\text{O}-\text{P}(=\text{O})\text{CH}_3(\text{OC}_6\text{H}_{11})$ . By 26 hours, *Figure 8*, the  $1250\text{ cm}^{-1}$  band is almost gone, appearing as but a shoulder on the side of the P-acid  $\nu$  P=O band near  $1200\text{ cm}^{-1}$ . The sample, after some 30 hours of exposure to moist air was dried for 3 days and the resultant infrared spectrum (*Figure 9*) showed the presence of **GF ACID**, cyclohexyl methylphosphonic acid (cyclohexyl hydrogen methylphosphonate),  $\text{CH}_3\text{P}=\text{O}(\text{OH})(\text{O}-\text{C}_6\text{H}_{11})$ .

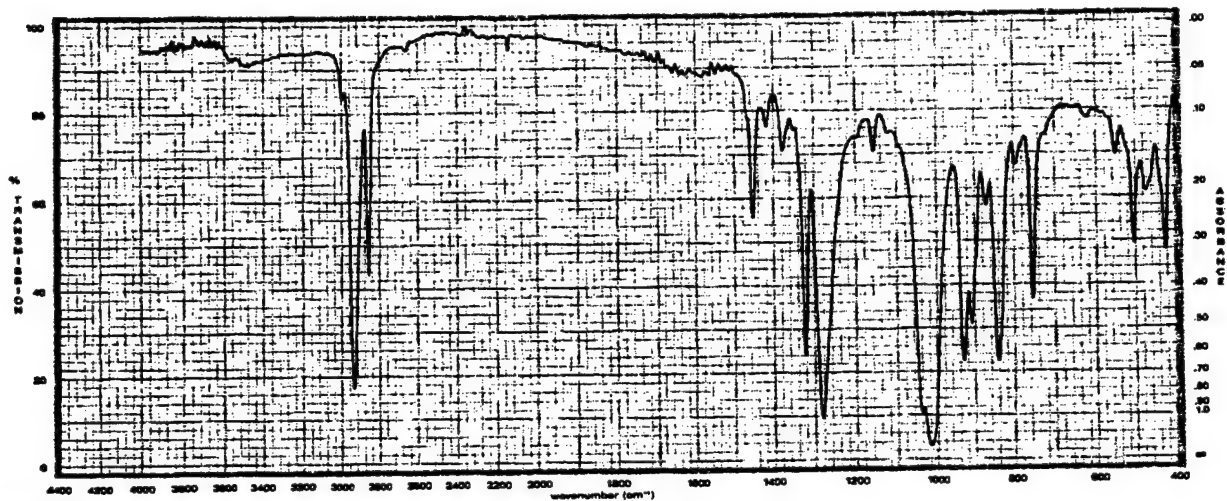


Figure 6 GF, LIQUID, CF/CsI, AFTER 2 HOURS

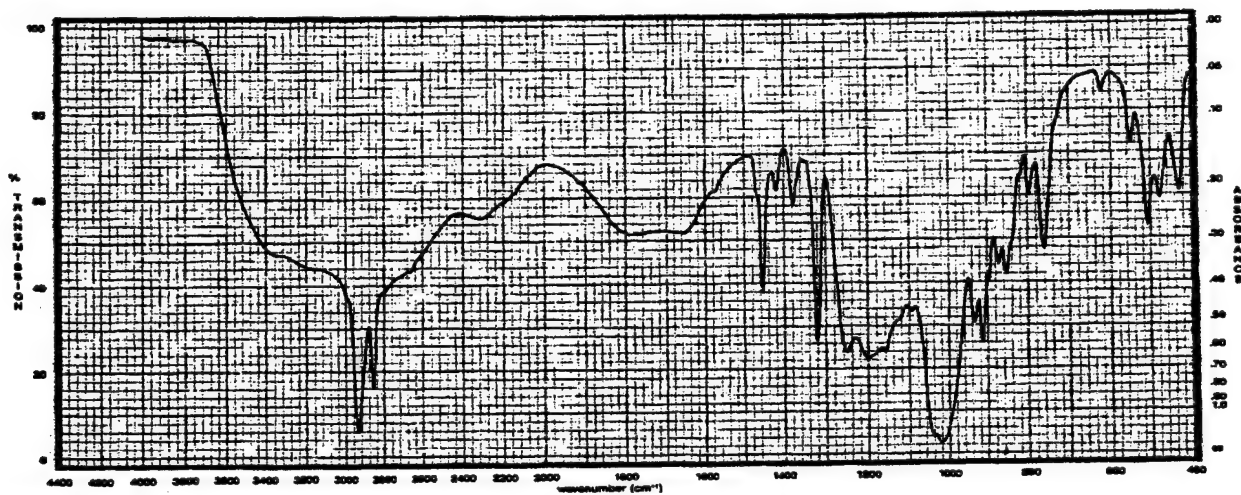


Figure 7 GF, LIQUID, CF/CsI, AFTER 22 HOURS

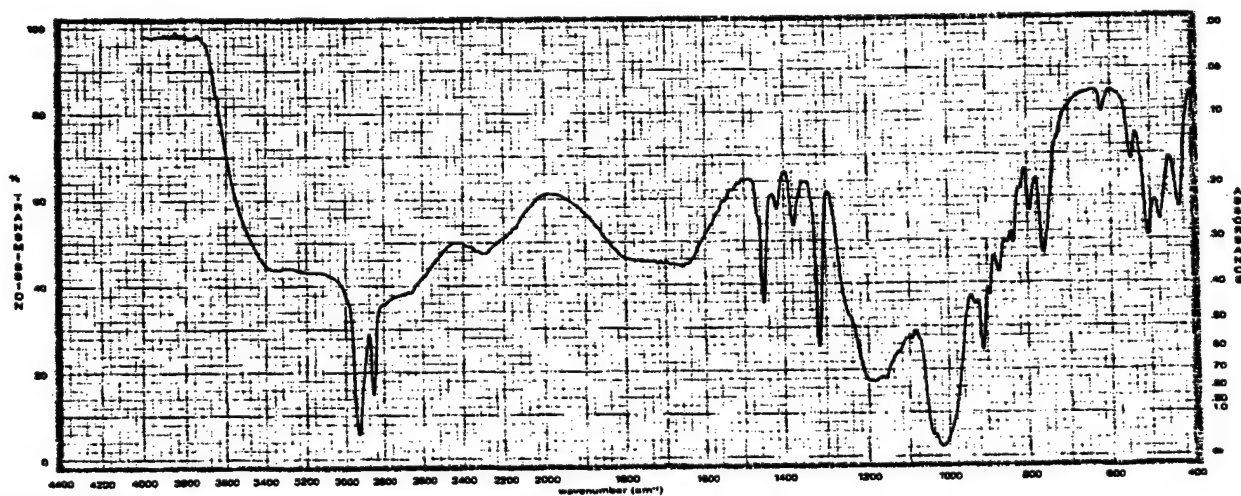


Figure 8 GF, LIQUID, CF/CsI, AFTER 26 HOURS

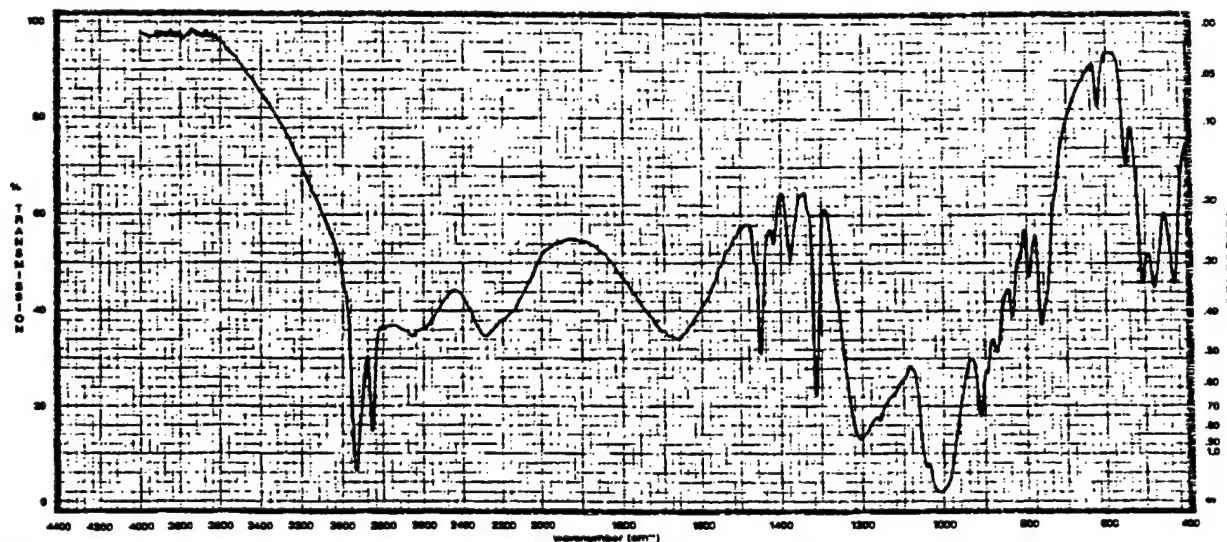


Figure 9 GF, LIQUID, CF/CsI, DRIED FOR 3 DAYS AFTER 30 HOURS IN LAB AIR

3.1.4 2-Methylcyclohexyl Methylphosphonofluoridate (EA 1356)  $\text{CH}_3\text{P}=\text{O}(\text{F})[\text{O}-(2-\text{CH}_3-\text{C}_6\text{H}_{10})]$

The infrared spectrum for 2-methylcyclohexyl methylphosphonofluoridate is given in *Figure 10*.

The infrared bands may be assigned as follows:  $2934\text{ cm}^{-1}$  ms and  $2861\text{ cm}^{-1}$  m aliphatic  $\nu\text{ CH}$ ,  $1452\text{ cm}^{-1}$  m ( $\delta\text{ CH}$ ),  $1418\text{ cm}^{-1}$  w ( $\delta_{\text{as}}\text{ P-CH}_3$ ),  $1319\text{ cm}^{-1}$  m ( $\delta_{\text{sy}}\text{ P-CH}_3$ ),  $1281\text{ cm}^{-1}$  ms ( $\nu\text{ P=O}$ ),  $1018\text{ cm}^{-1}$  s ( $\nu\text{ P-O-C}$ ),  $909\text{ cm}^{-1}$  m ( $\text{P-CH}_3$  rock),  $837\text{ cm}^{-1}$  m ( $\nu\text{ P-F}$ ), and  $752\text{ cm}^{-1}$  m ( $\nu\text{ P-C}$ ).

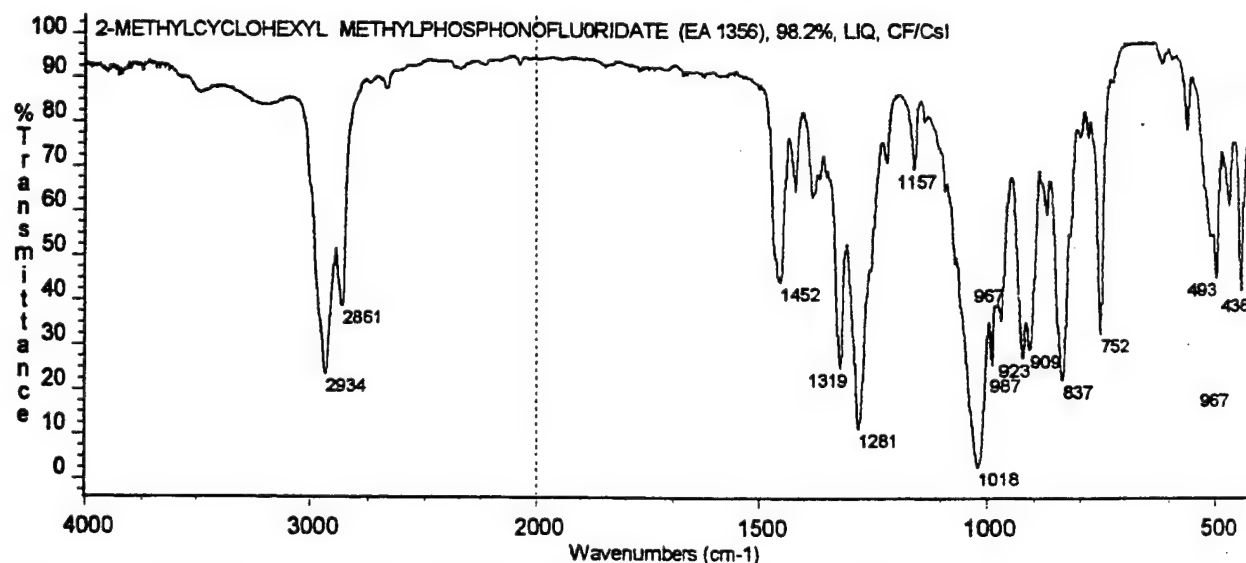
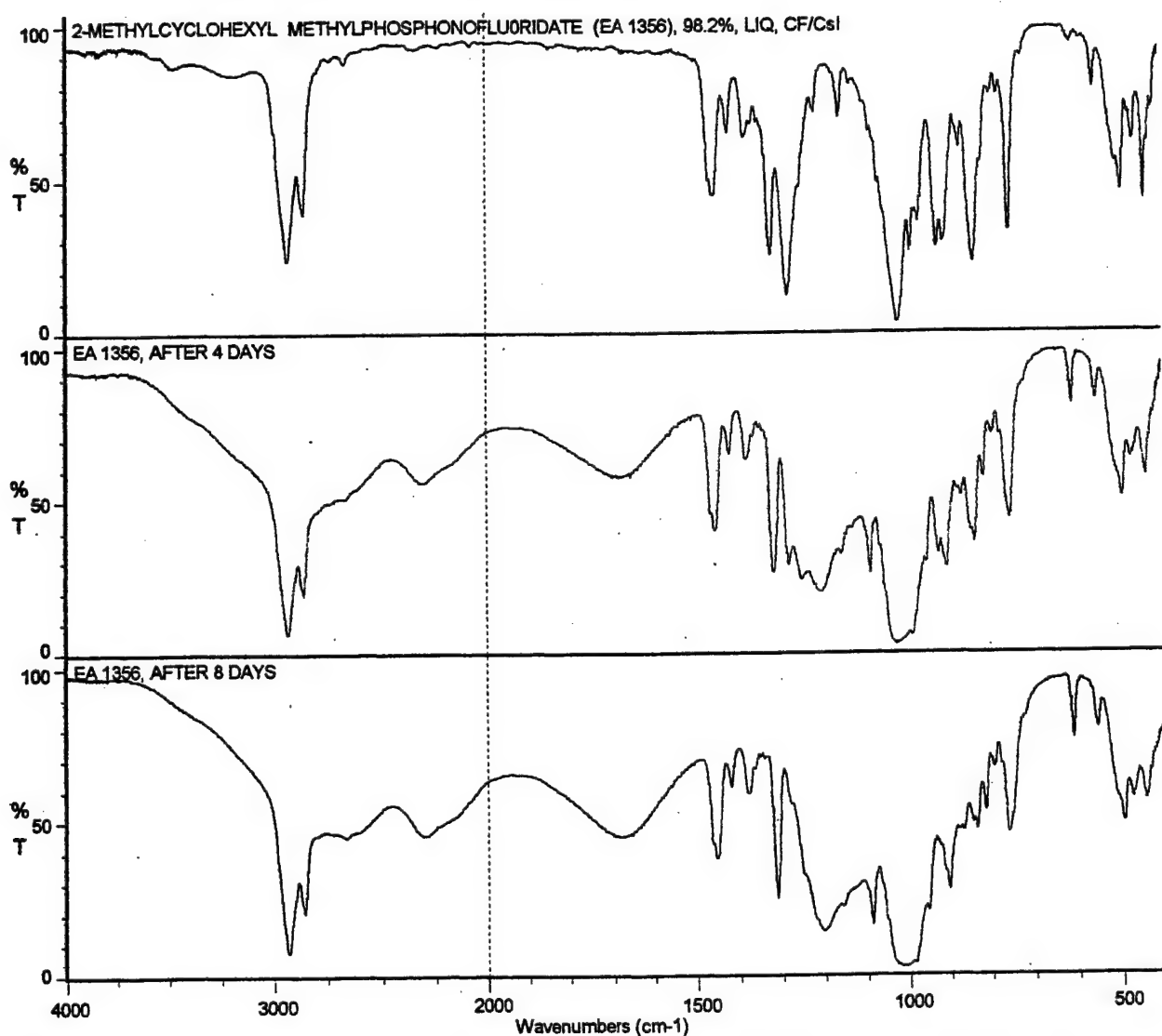
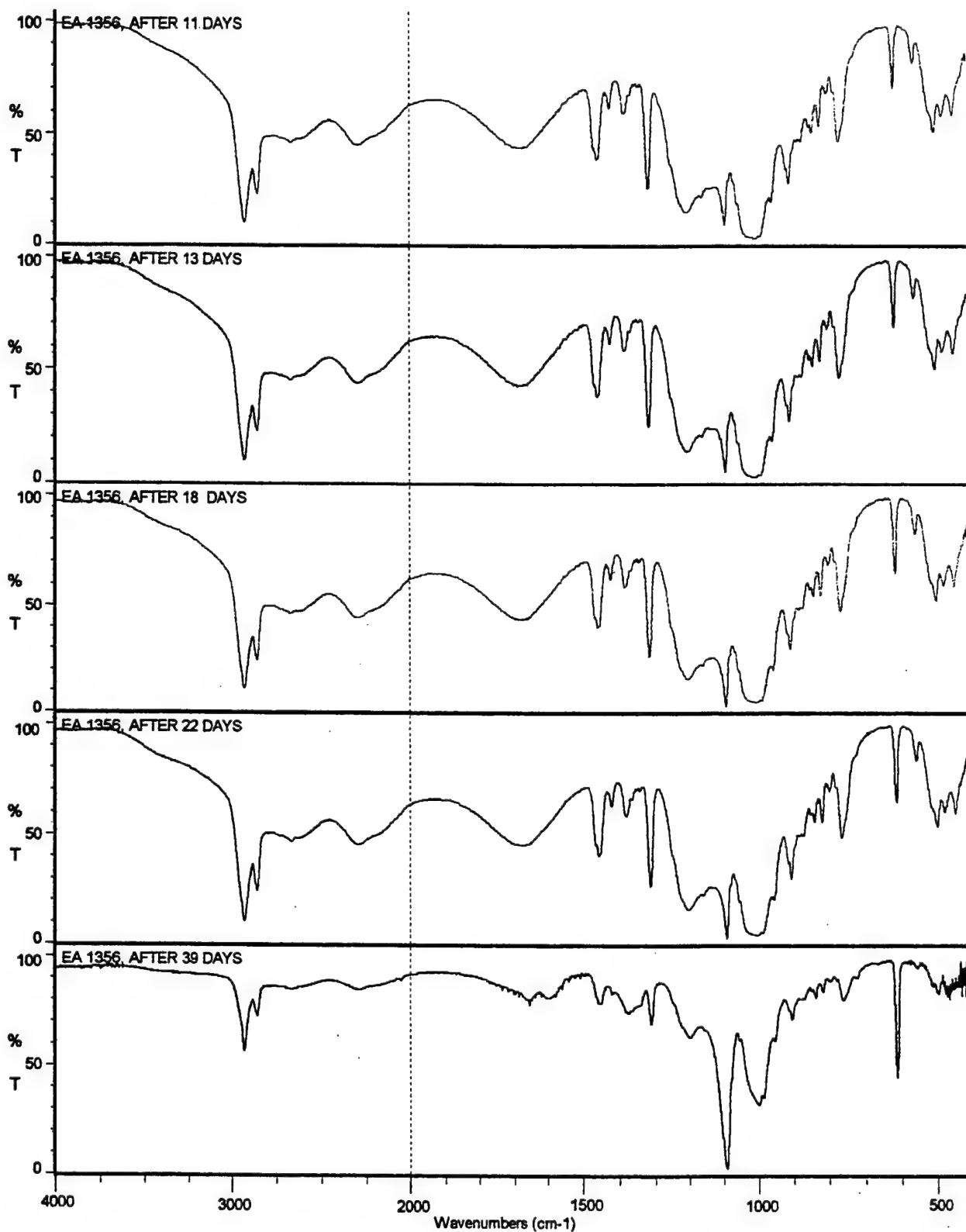


Figure 10 2-METHYLCYCLOHEXYL METHYLPHOSPHONOFUORIDATE, 98.2 %, LIQUID, CF/CsI

The effect of atmospheric moisture on the infrared spectrum of 2-methylcyclohexyl methylphosphonofluoridate is given in *Figures 11 and 11A*. After 4 days the spectrum shows the presence of a P-acid moiety with POH bands at ca 2600, 2259, 1670, and 1000  $\text{cm}^{-1}$ . A band at ca 1200  $\text{cm}^{-1}$  can be assigned to an acid  $\nu \text{P}=\text{O}$ . This trend continues through the 22 days of observation. Now the predominant species is 2-methylcyclohexyl methylphosphonic acid (2-methylcyclohexyl hydrogen methylphosphonate). By the 39<sup>th</sup> day, bands at ca 1097 and 610  $\text{cm}^{-1}$  are quite strong in the spectrum, and can be assigned to what is believed to be cesium sulfate,  $\text{Cs}_2\text{SO}_4$ .



**Figure 11 2-METHYLCYCLOHEXYL METHYLPHOSPHONOFUORIDATE (EA 1356), LIQUID, CF/CsI, EXPOSED TO ATMOSPHERIC MOISTURE**



**Figure 11 2-METHYLCYCLOHEXYL METHYLPHOSPHONOFUORIDATE (EA 1356), LIQUID, CF/CsI, EXPOSED TO ATMOSPHERIC MOISTURE (CONTINUED)**



### 3.1.5 Methyl Methylphosphonofluoridate (EA 1232)



The infrared spectrum for methyl methylphosphonofluoridate is given in *Figure 12*. The band assignments are as follows: 3003  $\text{cm}^{-1}$  w, 2965  $\text{cm}^{-1}$  w, 2932  $\text{cm}^{-1}$  w and 2860  $\text{cm}^{-1}$  vw ( $\nu$   $\text{CH}_3$ ), 1465  $\text{cm}^{-1}$  w ( $\delta$   $\text{CH}_3$ ), 1420  $\text{cm}^{-1}$  w ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ), 1324  $\text{cm}^{-1}$  ms ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ), 1282  $\text{cm}^{-1}$  s ( $\nu$  P=O), 1187  $\text{cm}^{-1}$  w ( $\text{OCH}_3$ ,  $\text{CH}_3$  rock), 1052  $\text{cm}^{-1}$  s ( $\nu$  P-O-C), 925  $\text{cm}^{-1}$  ms (P- $\text{CH}_3$  rock), 844  $\text{cm}^{-1}$  ms ( $\nu$  P-F), 815  $\text{cm}^{-1}$  m (POC), 733  $\text{cm}^{-1}$  m ( $\nu$  P-C), 502  $\text{cm}^{-1}$  m ( $\delta$  P=O ?).

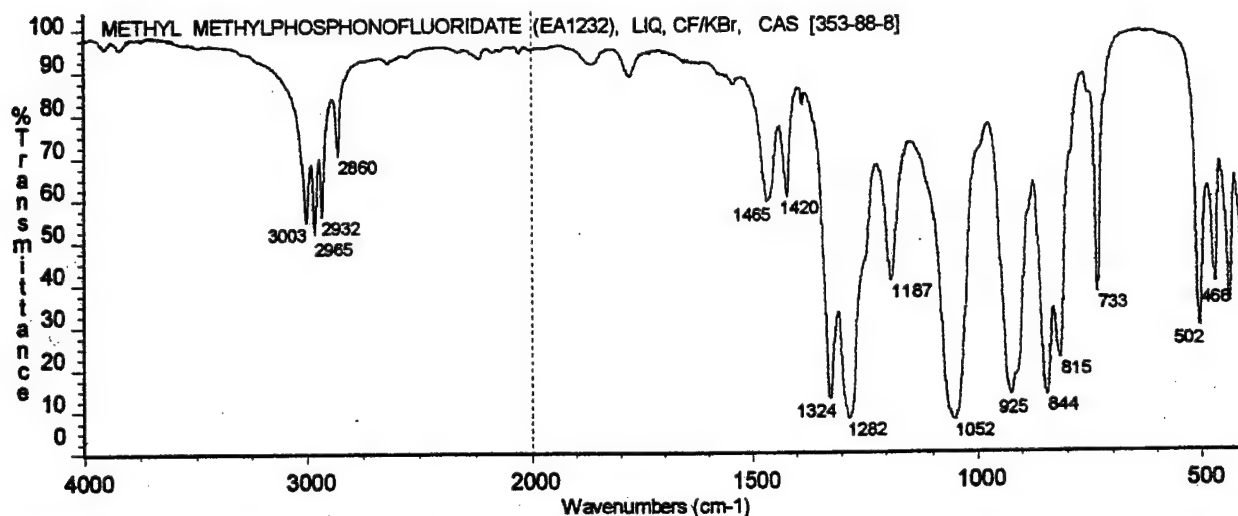
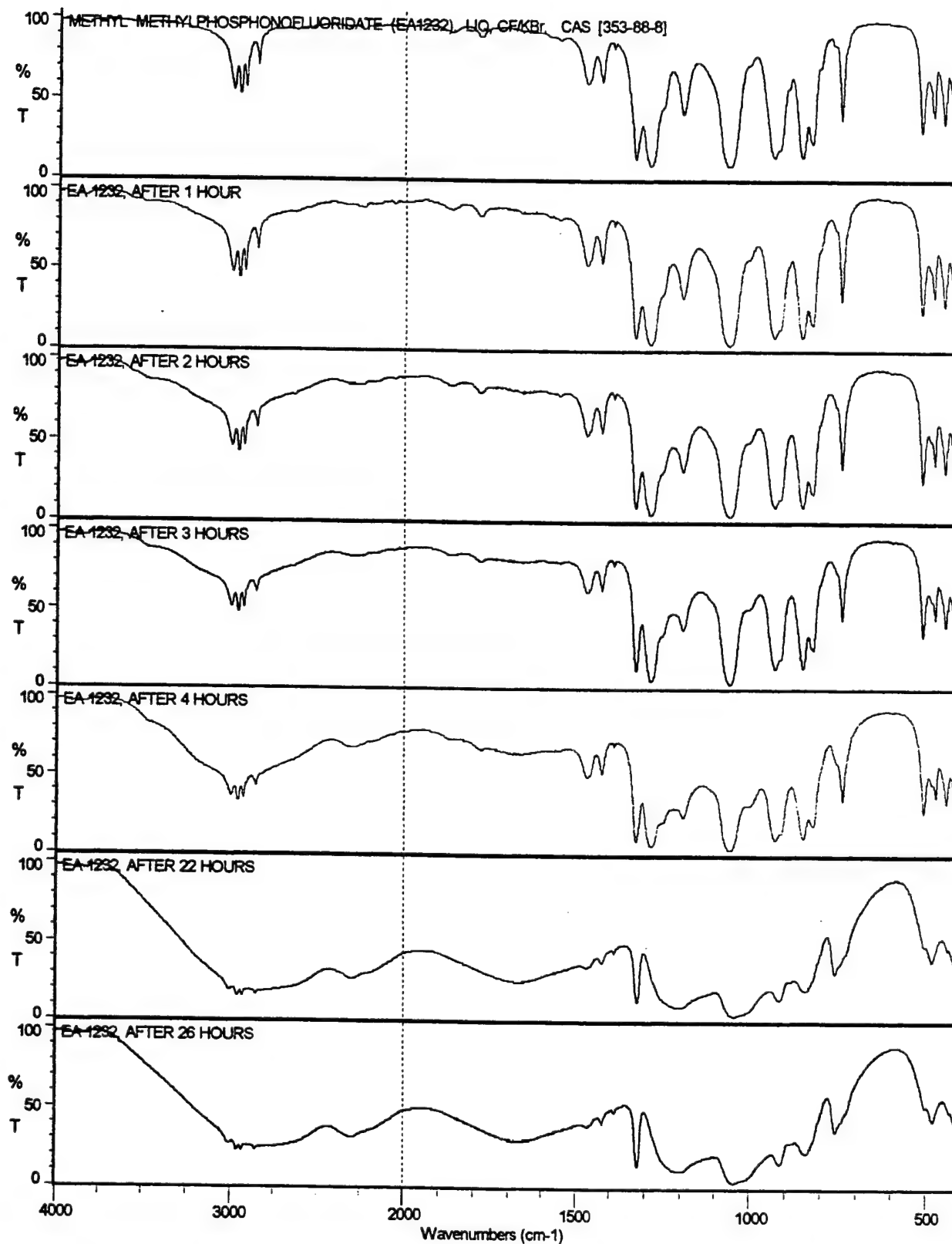


Figure 12 METHYL METHYLPHOSPHONOFLUORIDATE (EA 1232), LIQUID, CF/KBr

*Figure 13* shows the effect of atmospheric moisture on the thin liquid film of EA 1232 while between KBr windows for a period of 43 days. The broadening of the CH stretching band in the vicinity of 3000  $\text{cm}^{-1}$  after only 1 hour is indicative of the formation of the P-OH moiety. As time progresses bands indicative of the POH moiety (ca 3000, 2250, 1680 and 1000  $\text{cm}^{-1}$ ) become more predominant in the infrared spectrum. The band due to the P=O (1282  $\text{cm}^{-1}$ ) decreases to the 1200  $\text{cm}^{-1}$  region and the P-F band (844  $\text{cm}^{-1}$ ) disappears from the spectrum. The resultant spectrum gradually takes on the appearance of the P-acid,  $\text{CH}_3\text{P}=\text{O}(\text{OH})(\text{OCH}_3)$ , methyl hydrogen methylphosphonate (methyl methylphosphonic acid). Perhaps finally going to methylphosphonic acid as follows:





**Figure 13 METHYL METHYLPHOSPHONOFUORIDATE (EA 1232), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE**

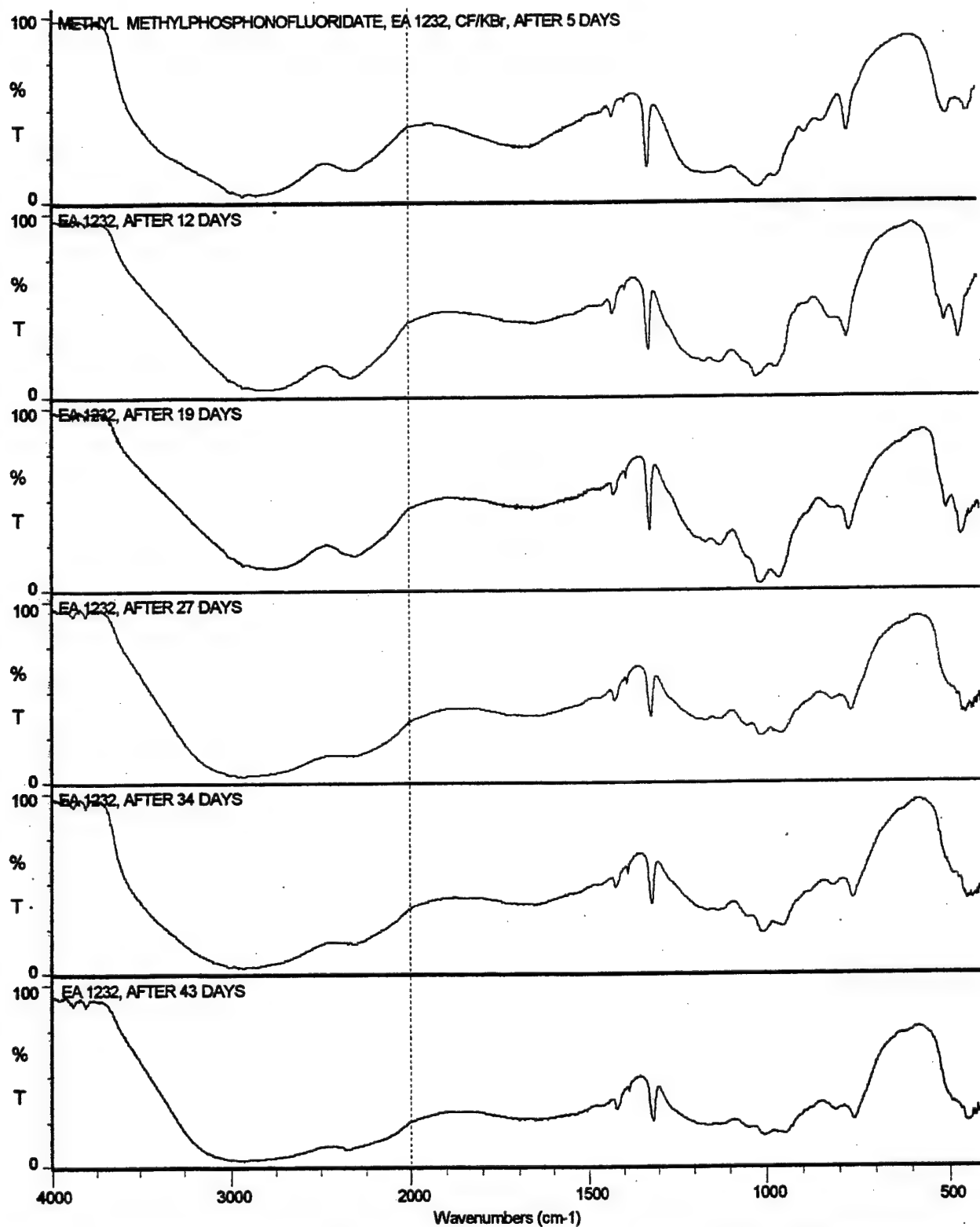
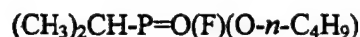
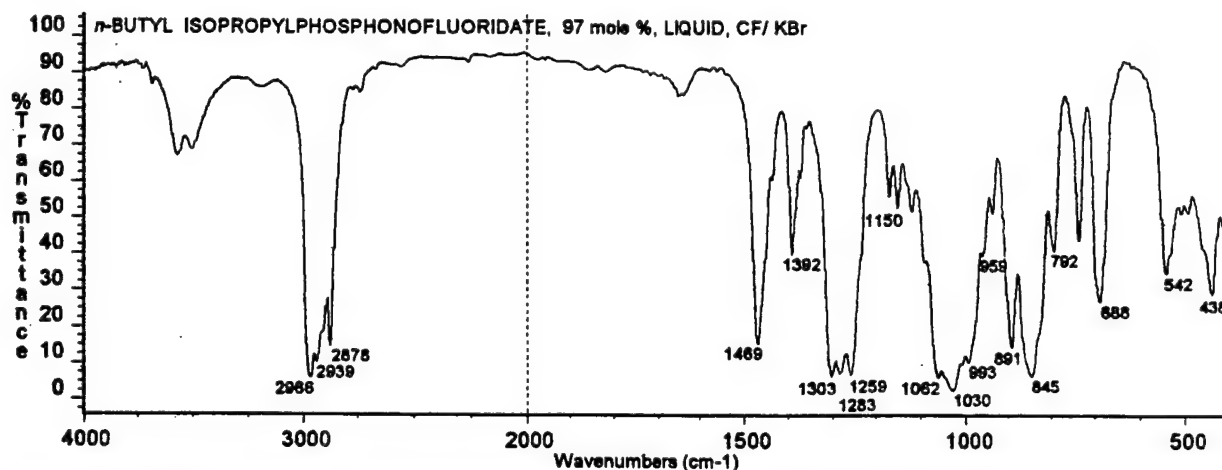


Figure 13 METHYL METHYLPHOSPHONOFUORIDATE (EA 1232), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

### 3.1.6 *n*-Butyl Isopropylphosphonofluoridate



The infrared spectrum of *n*-butyl isopropylphosphonofluoridate is given in *Figure 14*. The band assignments are as follows: ca 3500  $\text{cm}^{-1}$  w and ca 1650  $\text{cm}^{-1}$  vw (water), 2966  $\text{cm}^{-1}$  s, 2939  $\text{cm}^{-1}$  sh and 2878  $\text{cm}^{-1}$  ms ( $\nu$   $\text{CH}_3$  and  $\text{CH}_2$ ), 1469  $\text{cm}^{-1}$  ms and 1436  $\text{cm}^{-1}$  sh ( $\delta$   $\text{CH}_3$  and  $\text{CH}_2$ ), 1392  $\text{cm}^{-1}$  m and 1372  $\text{cm}^{-1}$  vw ( $\delta_{\text{sy}}$   $\text{CH}_3$ ), 1358  $\text{cm}^{-1}$  vw ( $\delta$   $\text{CH}$ , isopropyl moiety), 1303  $\text{cm}^{-1}$  ms (P-isopropyl ?), 1283 and 1259  $\text{cm}^{-1}$  ms (the average of these two frequencies is 1271  $\text{cm}^{-1}$ , the  $\nu$   $\text{P}=\text{O}$  has a calculated value of 1272  $\text{cm}^{-1}$ ), 1169  $\text{cm}^{-1}$  w, 1150  $\text{cm}^{-1}$  w and 1119  $\text{cm}^{-1}$  w (may be characteristic of the P-O-butyl moiety), 1062  $\text{cm}^{-1}$  sh and 1030  $\text{cm}^{-1}$  s ( $\nu$  P-O-C), 993  $\text{cm}^{-1}$  ms ( $\nu$  C-C of P-O-butyl), 891  $\text{cm}^{-1}$  ms ( $\text{CH}_3$  rock of the isopropyl moiety), 845  $\text{cm}^{-1}$  ms ( $\nu$  P-F), 792  $\text{cm}^{-1}$  m (POC ?), 688  $\text{cm}^{-1}$  m ( $\nu$  P-C ?).



**Figure 14** *n*-BUTYL ISOPROPYLPHOSPHONOFUORIDATE, 97 MOLE %, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin film of *n*-butyl isopropylphosphonofluoridate while between KBr windows is given in *Figure 15*. The effect of moisture on the compound can be seen after 22 hours when bands indicative of a POH moiety become evident near 2750, 2250 and 1680  $\text{cm}^{-1}$ . By 5 days the POH bands are even more pronounced and the P-F band is almost completely gone. The hydrolysis study continued for 13 days and the film between the KBr windows was dried for 24 hours in the dry air purge of the instrument. This was repeated until the resultant film had been dried for some 16 days. The hydrolysis product may be represented by the structure  $(\text{CH}_3)_2\text{CH}-\text{P}=\text{O}(\text{OH})(\text{O}-n\text{-Butyl})$ ,

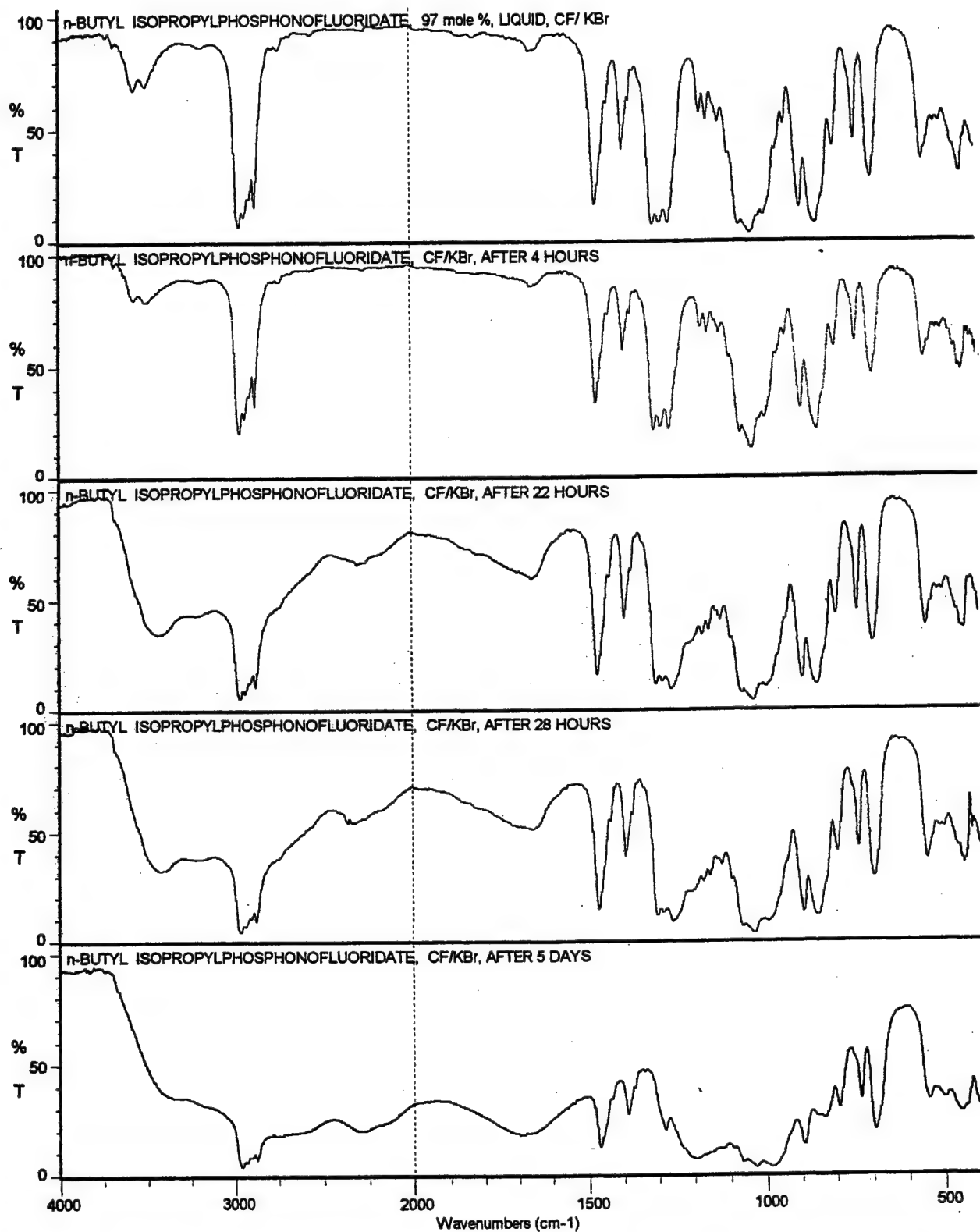


Figure 15: *n*-BUTYL ISOPROPYLPHOSPHONOFUORIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

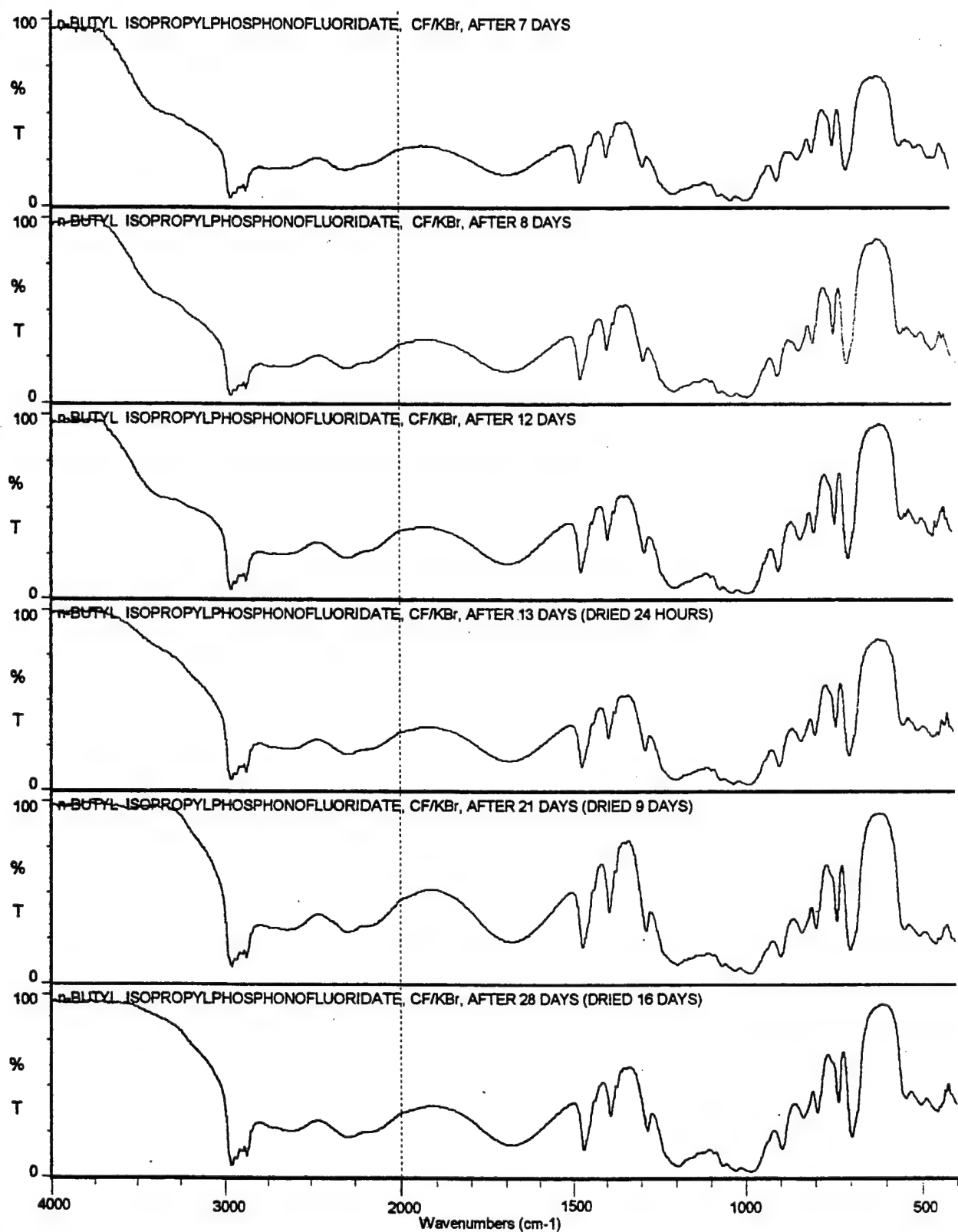
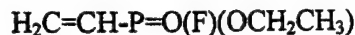


Figure 15. *n*-BUTYL ISOPROPYLPHOSPHONOFUORIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

*n*-butyl hydrogen isopropylphosphonate (*n*-butyl isopropylphosphonic acid).

### 3.1.7 Ethyl Vinylphosphonofluoridate



The infrared spectrum of ethyl vinylphosphonofluoridate is given in *Figure 16*. The band assignments are as follows: 3096  $\text{cm}^{-1}$  vw ( $\nu_{\text{as}}=\text{CH}_2$ ), 3049  $\text{cm}^{-1}$  vw ( $\nu_{\text{sy}}=\text{CH}_2$ ), 2989  $\text{cm}^{-1}$  w, 2938  $\text{cm}^{-1}$  vw and 2916  $\text{cm}^{-1}$  vw ( $\nu$  CH of POEt), 1616  $\text{cm}^{-1}$  vw ( $\nu$  C=C), 1481  $\text{cm}^{-1}$  vw ( $\delta$  O-CH<sub>2</sub>), 1447  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$  CH<sub>3</sub>), 1403  $\text{cm}^{-1}$  w ( $\omega$  CH<sub>2</sub>), 1372  $\text{cm}^{-1}$  vw ( $\delta_{\text{sy}}$  CH<sub>3</sub>), 1293  $\text{cm}^{-1}$  ms ( $\nu$  P=O), 1166  $\text{cm}^{-1}$  w and 1098  $\text{cm}^{-1}$  w (CH<sub>3</sub> rock, characteristic of POEt), 1043  $\text{cm}^{-1}$  s ( $\nu$  P-O-C), 983  $\text{cm}^{-1}$  m ( $\nu$  C-C of POEt, a shoulder near 965  $\text{cm}^{-1}$  on the side of the 983  $\text{cm}^{-1}$  band may be due to the *trans* CH wag), 858  $\text{cm}^{-1}$  ms ( $\nu$  P-F), 796  $\text{cm}^{-1}$  m (POC).

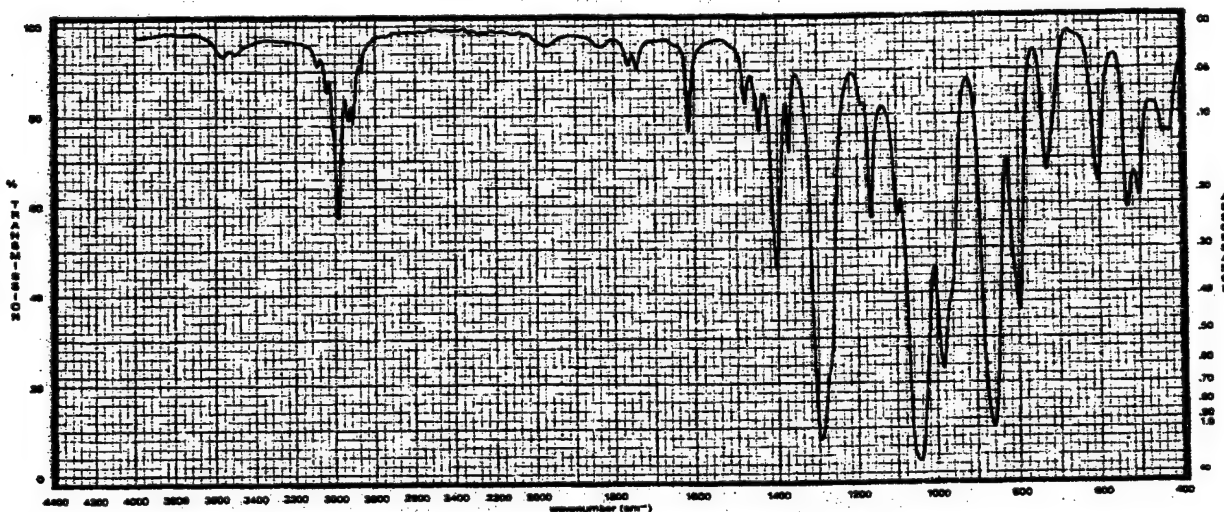


Figure 16 ETHYL VINYLPHOSPHONOFUORIDATE, 99.5 MOLE %, LIQUID, CF/CsI

The effect of atmospheric moisture on the thin film of ethyl vinylphosphonofluoridate is given in *Figures 17A and 17B*. After seven days the infrared spectrum is that of mainly a P-acid with perhaps a trace of residual P=F at 863  $\text{cm}^{-1}$ . The spectrum after 20 days is essentially that of ethyl hydrogen vinylphosphonate (ethyl vinylphosphonic acid),  $\text{CH}_2=\text{CH}-\text{P}=\text{O}(\text{OH})(\text{OC}_2\text{H}_5)$ , which has bands at 2987  $\text{cm}^{-1}$  vw and 2910  $\text{cm}^{-1}$  vw ( $\nu$  CH), ca 2700  $\text{cm}^{-1}$  m broad, 2290  $\text{cm}^{-1}$  m broad and 1660  $\text{cm}^{-1}$  m broad (indicative of a POH moiety), 1616  $\text{cm}^{-1}$  vw ( $\nu$  C=C), 1481  $\text{cm}^{-1}$  vw ( $\delta$  OCH<sub>2</sub>), 1447  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$  CH<sub>3</sub>),

1406  $\text{cm}^{-1}$  w ( $\omega$   $\text{OCH}_2$ ), 1372  $\text{cm}^{-1}$  vvw ( $\delta_{\text{as}}$   $\text{CH}_3$ ), 1280  $\text{cm}^{-1}$  w ( $=\text{CH}$  rock), 1200  $\text{cm}^{-1}$  ms ( $\nu$   $\text{P}=\text{O}$ ), 1167  $\text{cm}^{-1}$  vw and 1091  $\text{cm}^{-1}$  vw ( $\text{CH}_3$  rock, characteristic of POEt), 1035  $\text{cm}^{-1}$  s ( $\nu$   $\text{P}-\text{O}-\text{C}$ ), 989  $\text{cm}^{-1}$  s [ $\nu$   $\text{P}-\text{O}(\text{H})$  and  $\nu$   $\text{C}-\text{C}$  of POEt, ca 980 shoulder (may also have some contribution from the *trans*  $=\text{CH}$  wag ?)], 800  $\text{cm}^{-1}$  w POC.

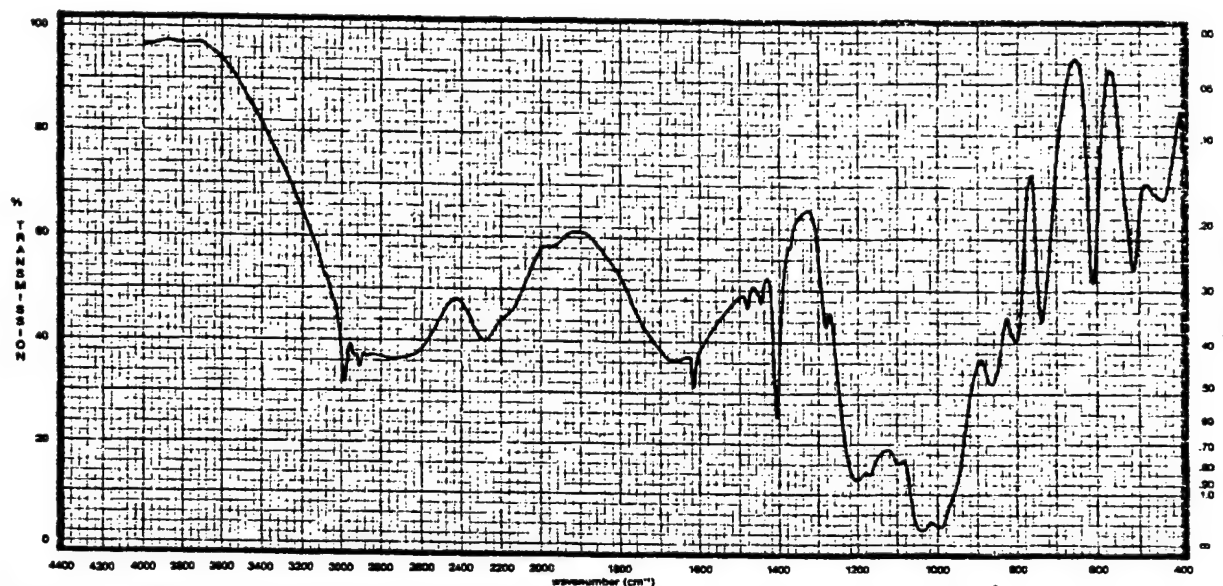


Figure 17A ETHYL VINYLPHOSPHONOFUORIDATE, LIQUID, CF/CsI AFTER 7 DAYS

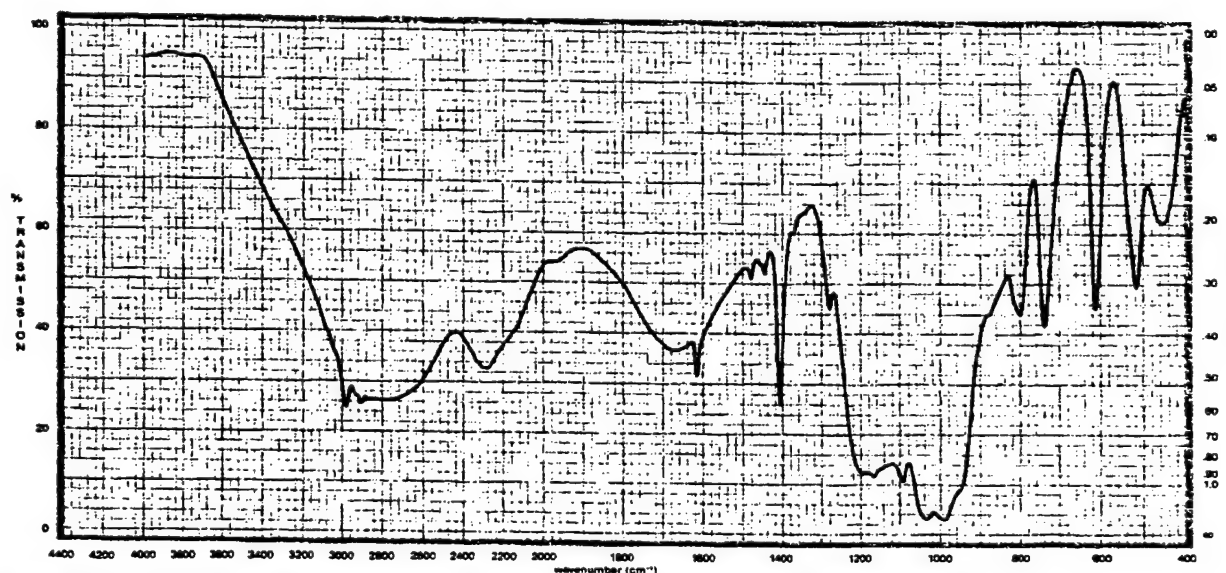


Figure 17B ETHYL VINYLPHOSPHONOFUORIDATE, LIQUID, CF/CsI, AFTER 20 DAYS



### 3.1.8 Trimethylsilyl Methylphosphonocyanide



The infrared spectrum for trimethylsilyl methylphosphonocyanide, is presented in *Figure 18*.

The bands may be assigned as follows:  $2965\text{ cm}^{-1}$  m ( $\nu_{\text{as}} \text{CH}_3$ ),  $2920\text{ cm}^{-1}$  w ( $\nu_{\text{sy}} \text{CH}_3$ ),  $2202\text{ cm}^{-1}$  ms ( $\nu \text{C}\equiv\text{N}$ ),  $2081\text{ cm}^{-1}$  vvw ( $\nu \text{C}\equiv\text{N}$  from HCN, some broadening above the  $2965\text{ cm}^{-1}$  band may also be due to the presence of HCN),  $1411\text{ cm}^{-1}$  w ( $\delta_{\text{as}} \text{P-CH}_3$  and  $\delta_{\text{as}} \text{Si-CH}_3$ ),  $1312\text{ cm}^{-1}$  ms ( $\delta_{\text{sy}} \text{P-CH}_3$ ),  $1272$  and  $1260\text{ cm}^{-1}$  s split band (the  $1272\text{ cm}^{-1}$  band is probably the  $\nu \text{P}=\text{O}$  since the calculated value<sup>a</sup> for this vibration would be  $1274\text{ cm}^{-1}$ , while the  $1260\text{ cm}^{-1}$  band may be assigned to the  $\delta_{\text{sy}} \text{Si-CH}_3$ ),  $1048\text{ cm}^{-1}$  s ( $\nu \text{P-O-C}$ ),  $889\text{ cm}^{-1}$  m ( $\text{P-CH}_3$  rock),  $853\text{ cm}^{-1}$  s and  $783\text{ cm}^{-1}$  ms ( $\text{Si-CH}_3$  rocking and  $\nu \text{Si-C}$ ),  $764\text{ cm}^{-1}$  m ( $\nu \text{P-C ?}$ ),  $596\text{ cm}^{-1}$  m ( $\text{P-CN ?}$ ).

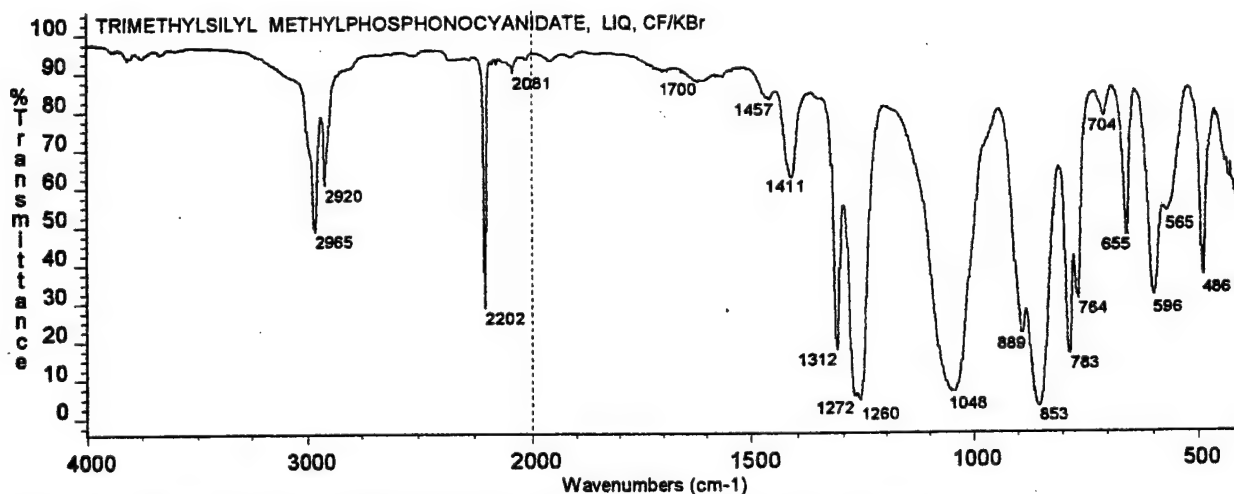
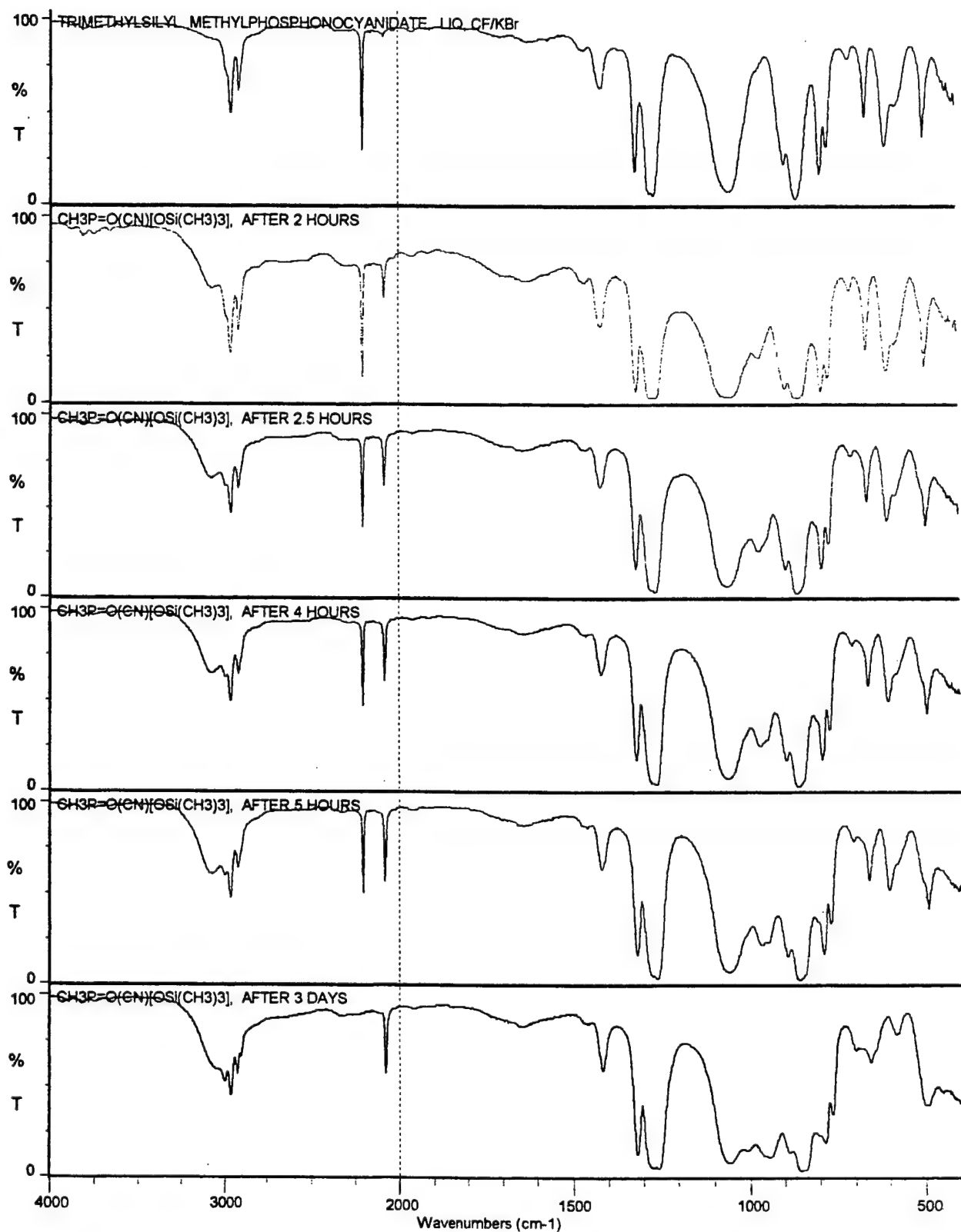


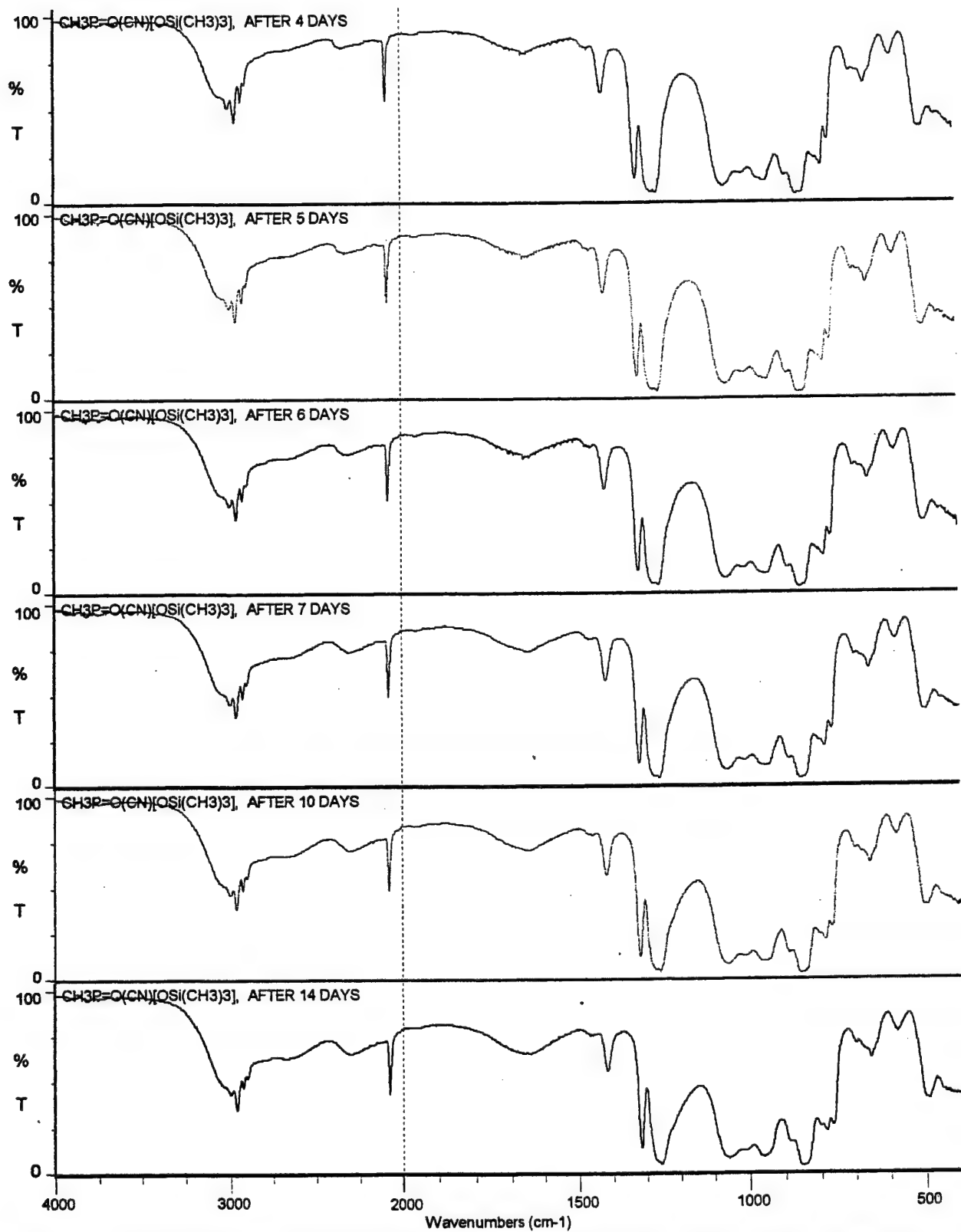
Figure 18 TRIMETHYLSILYL METHYLPHOSPHONOCYANIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on the thin film of trimethylsilyl methylphosphonocyanide while between KBr windows is given in *Figure 19*. As time progresses to 5 hours of exposure to atmospheric moisture, the infrared spectrum shows an increase in the intensities of the bands at  $3074\text{ cm}^{-1}$  w and  $2080\text{ cm}^{-1}$  w ( $\text{H-C}\equiv\text{N}$ ) and a corresponding decrease in the intensity of the  $\text{P-C}\equiv\text{N}$  at  $2202\text{ cm}^{-1}$ . A new band appears at  $964\text{ cm}^{-1}$  which may be assigned to a pyro  $\text{P-O-P}$  moiety. No bands

<sup>a</sup> The calculation of the phosphoryl frequency is described in L. C. Thomas, "Interpretation of the Infrared Spectra of Organophosphorus Compounds," Heyden, New York, 1974.



**Figure 19** TRIMETHYLSILYL METHYLPHOSPHONOCYANIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE



**Figure 19** TRIMETHYLSILYL METHYLPHOSPHONOCYANIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

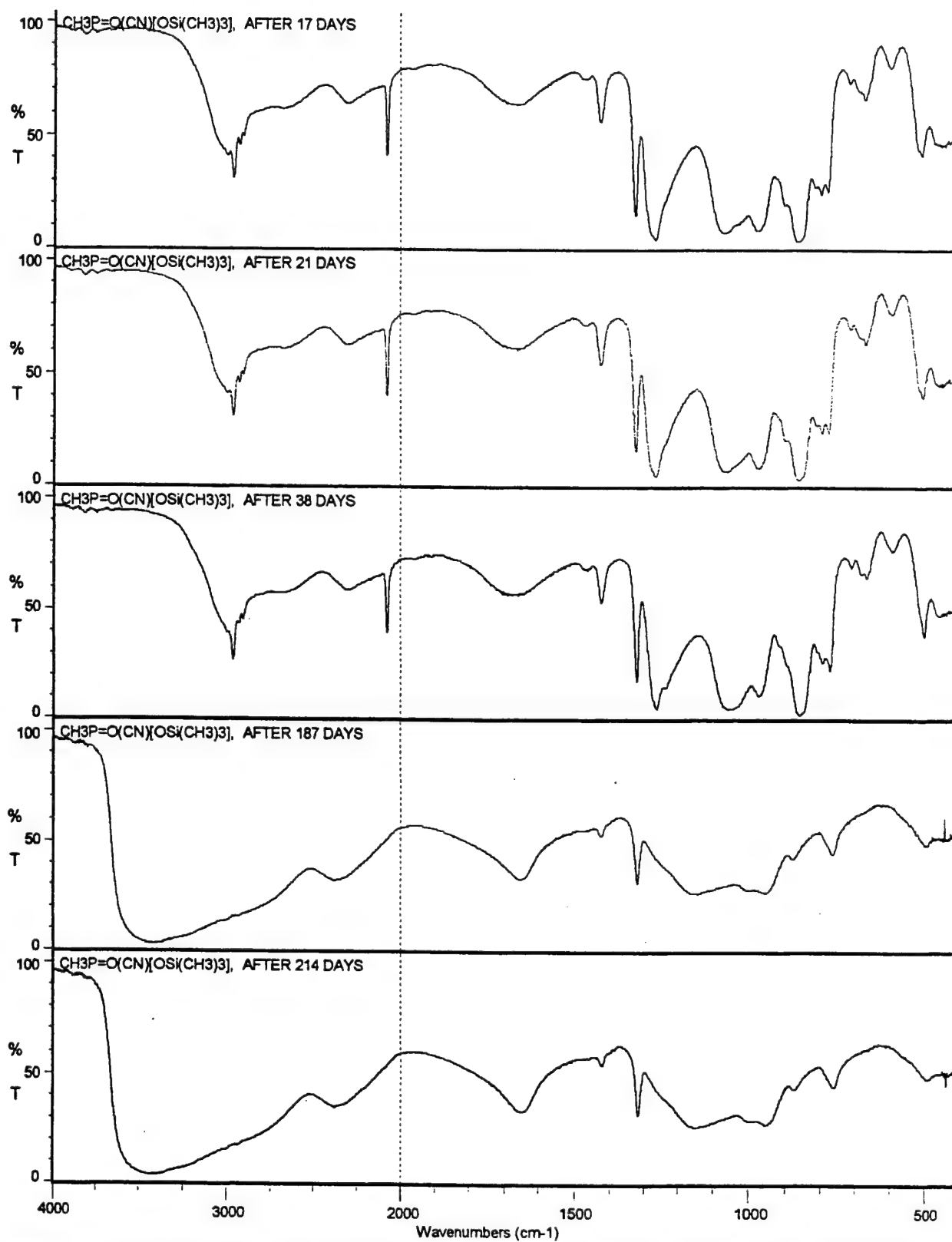


Figure 19 **TRIMETHYLSILYL METHYLPHOSPHONOCYANIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)**

assignable to the P-OH group are yet visible in the spectrum. Thus, a pyro compound such as  $[(CH_3)_3SiO]CH_3P(=O)-O-P(=O)CH_3[OSi(CH_3)_3]$  may be forming. As time progresses the P-C≡N band at  $2202\text{ cm}^{-1}$  disappears and the band due to HCN is left at  $2080\text{ cm}^{-1}$ . This is the case up to 38 days. However, since the 3 days time period, some bands due to the P-OH moiety have also been creeping into the spectra. At the 38 day mark two moieties seem to be predominant in the spectra, namely, a P-acid and the aforementioned pyro compound. The acid may be  $CH_3P=O(OH)[OSi(CH_3)_3]$ . Between the 38 day and the 187 day periods further hydrolysis of the compound(s) appears to have occurred to form a wet methylphosphonic acid,  $CH_3P=O(OH)_2$ . Compare the spectra after 187 or 214 days to *Figure 20* which is the spectrum of methylphosphonic acid to which some water had been added.

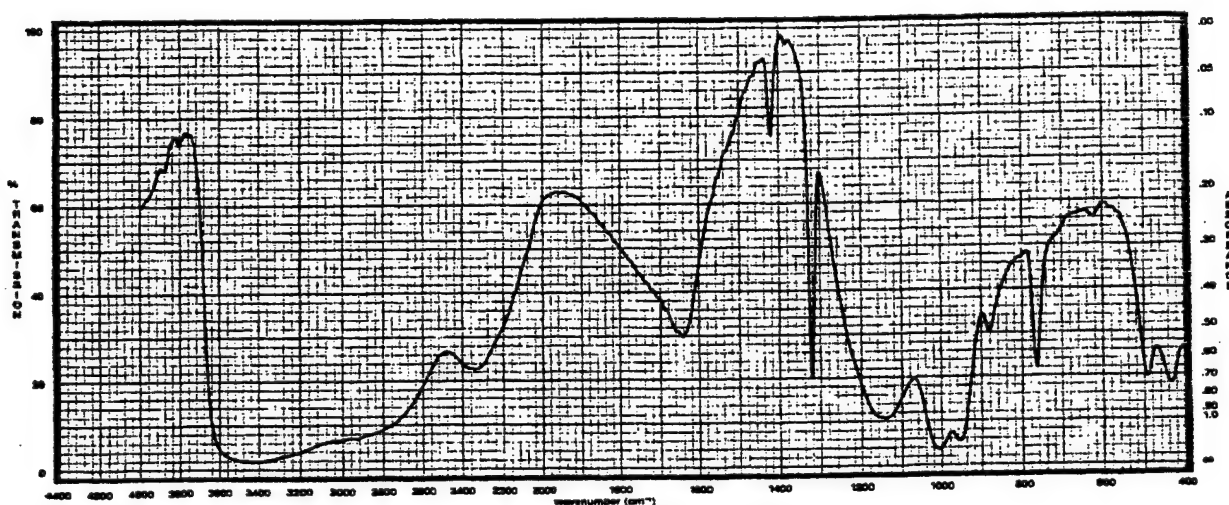


Figure 20 WET METHYLPHOSPHONIC ACID, FILM BETWEEN KBr DISCS

### 3.1.9 Ethyl N,N-Dimethylphosphoramidocyanidate (GA) $(CH_3)_2N-P=O(C\equiv N)(OCH_2CH_3)$

The infrared spectrum of GA, ethyl N,N-dimethylphosphoramidocyanidate, is given in *Figure 21*. Band assignments for GA are as follows:  $2988\text{ cm}^{-1}$  m,  $2942\text{ cm}^{-1}$  m,  $2912\text{ cm}^{-1}$  m,  $2864\text{ cm}^{-1}$  w and  $2826\text{ cm}^{-1}$  w (aliphatic  $\nu$  CH),  $2195\text{ cm}^{-1}$  m ( $\nu$  C≡N),  $1812\text{ cm}^{-1}$  vvw ( $1030 + 788 = 1818$  ?),  $1734\text{ cm}^{-1}$  vvw ( $1006 + 731 = 1737$  ?),  $1481\text{ cm}^{-1}$  m ( $\delta$  OCH<sub>2</sub>),  $1459\text{ cm}^{-1}$  m ( $\delta$  CH<sub>3</sub>),  $1394\text{ cm}^{-1}$  w ( $\omega$  OCH<sub>2</sub>,  $\delta_{sy}$  CH<sub>3</sub>),  $1321\text{ cm}^{-1}$  ms [ $\dot{P}N(CH_3)_2$ ],  $1269\text{ cm}^{-1}$  s ( $\nu$  P=O,  $1181\text{ cm}^{-1}$  m [ $PN(CH_3)_2$ ],  $1165\text{ cm}^{-1}$  w and  $1098\text{ cm}^{-1}$

w (characteristic of POEt, CH<sub>3</sub> rock), 1068 cm<sup>-1</sup> sh [PN(CH<sub>3</sub>)<sub>2</sub>], 1030 cm<sup>-1</sup> s (ν P-O-C), 1006 cm<sup>-1</sup> s (ν P-N-C), 974 cm<sup>-1</sup> m (ν C-C of P-O-Et), 788 cm<sup>-1</sup> m (POC), 731 cm<sup>-1</sup> m (PNC), 595 cm<sup>-1</sup> m (P-C≡N?).

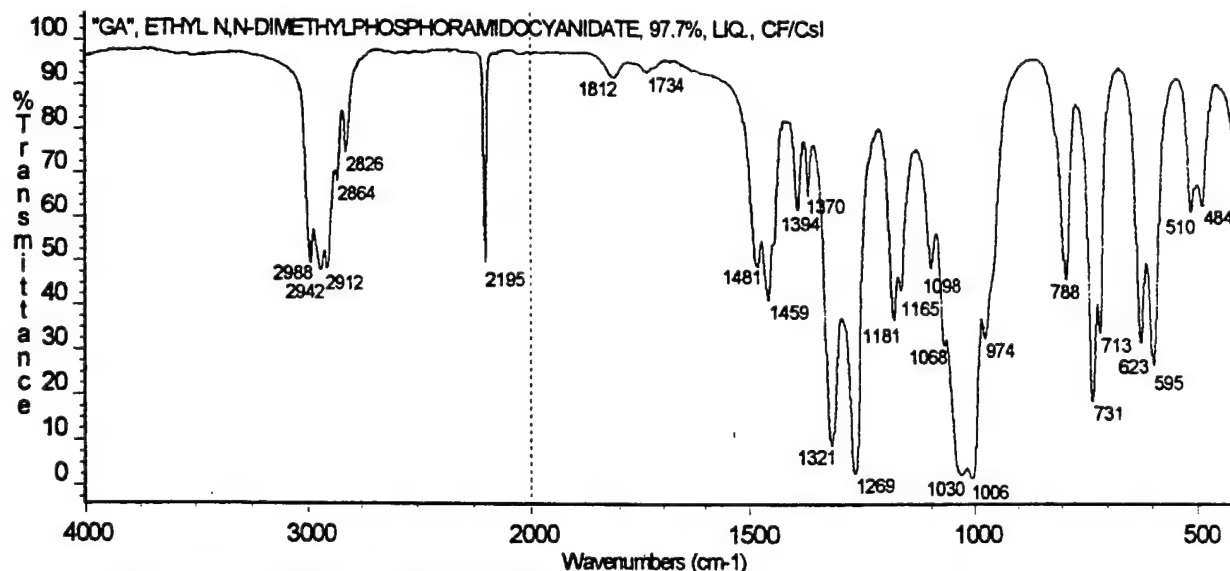


Figure 21 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQ., CF/CsI

The effect of atmospheric moisture on the infrared spectra of GA is given in *Figure 22*. As GA hydrolyzes there is a gradual decrease in the intensity of the ν C≡N band at 2195 cm<sup>-1</sup>. After 14 days no ν C≡N is present in the infrared spectrum. Bands are now observed at 1315 cm<sup>-1</sup> ms, 1188 cm<sup>-1</sup> w, 1006 cm<sup>-1</sup> s and 709 cm<sup>-1</sup> m [PN(CH<sub>3</sub>)<sub>2</sub>]; 1265 cm<sup>-1</sup> s (ν P=O); 1165 cm<sup>-1</sup> vw (POEt), 1052 cm<sup>-1</sup> ms (ν P-O-C, 985 cm<sup>-1</sup> sh (ν CC of POEt) and 796 cm<sup>-1</sup> w (POC). Bands at 1093 s and 613 w are due to the formation of what is believed to be cesium sulfate, Cs<sub>2</sub>SO<sub>4</sub>, from the cesium iodide windows. An infrared band at 932 cm<sup>-1</sup> s is assigned to a P-O-P stretching vibration from a pyro moiety such as (EtO) (CH<sub>3</sub>)<sub>2</sub> N-P(=O)-O-P(=O)N(CH<sub>3</sub>)<sub>2</sub> (OEt), which we shall call "GA PYRO" for a short name, or more properly *sym*-bis(dimethylamido) diethyl pyrophosphate or bis(ethyl N,N-dimethylphosphoramidic) anhydride. The pyro band at 932 cm<sup>-1</sup> shows up earlier between the 3 and 7 day time interval. The pyro compound appears to be present even after some 100 days. The infrared spectrum for an authentic sample of the "GA PYRO" is presented in *Figure 23*. The spectrum for GA PYRO shows the following bands:

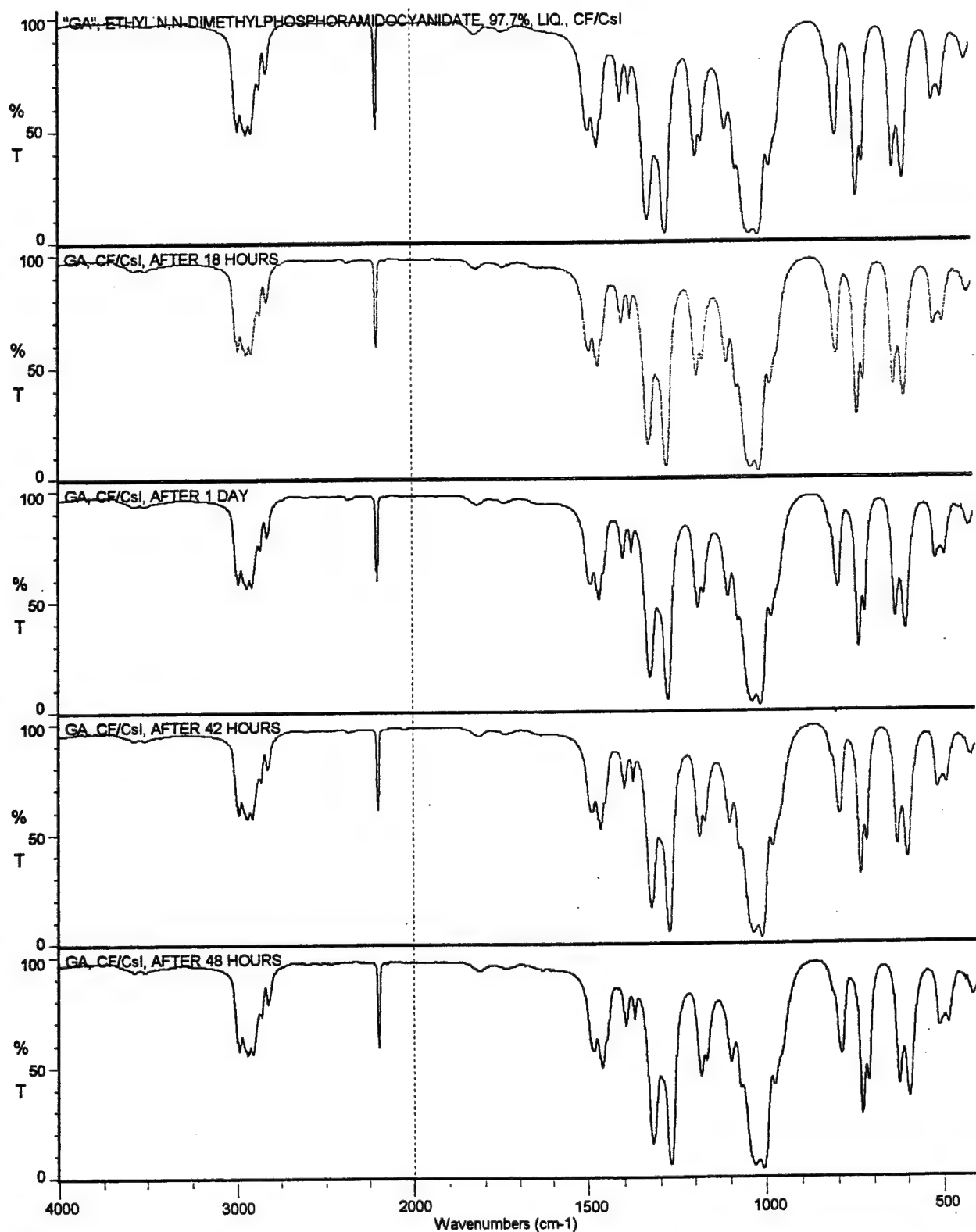
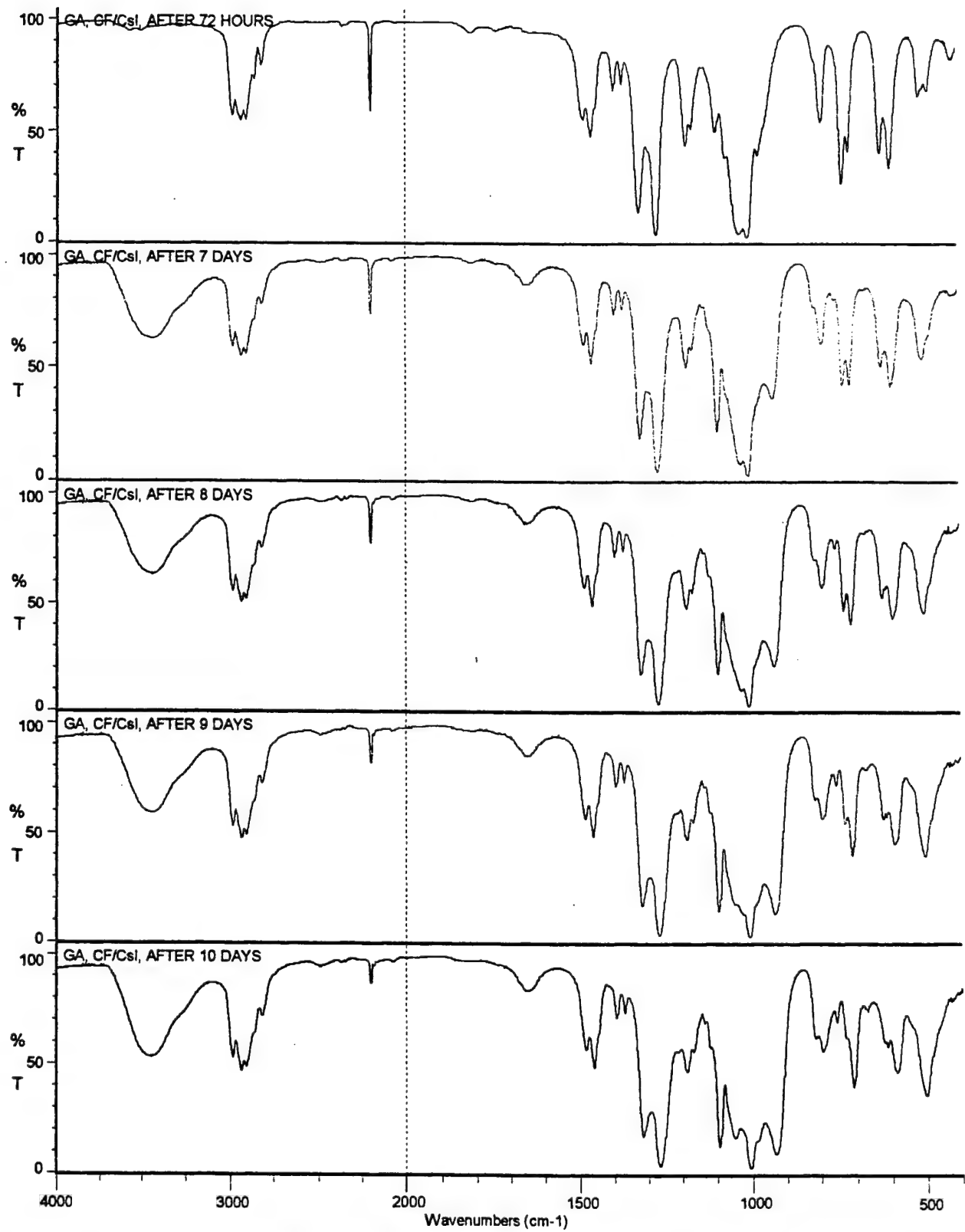
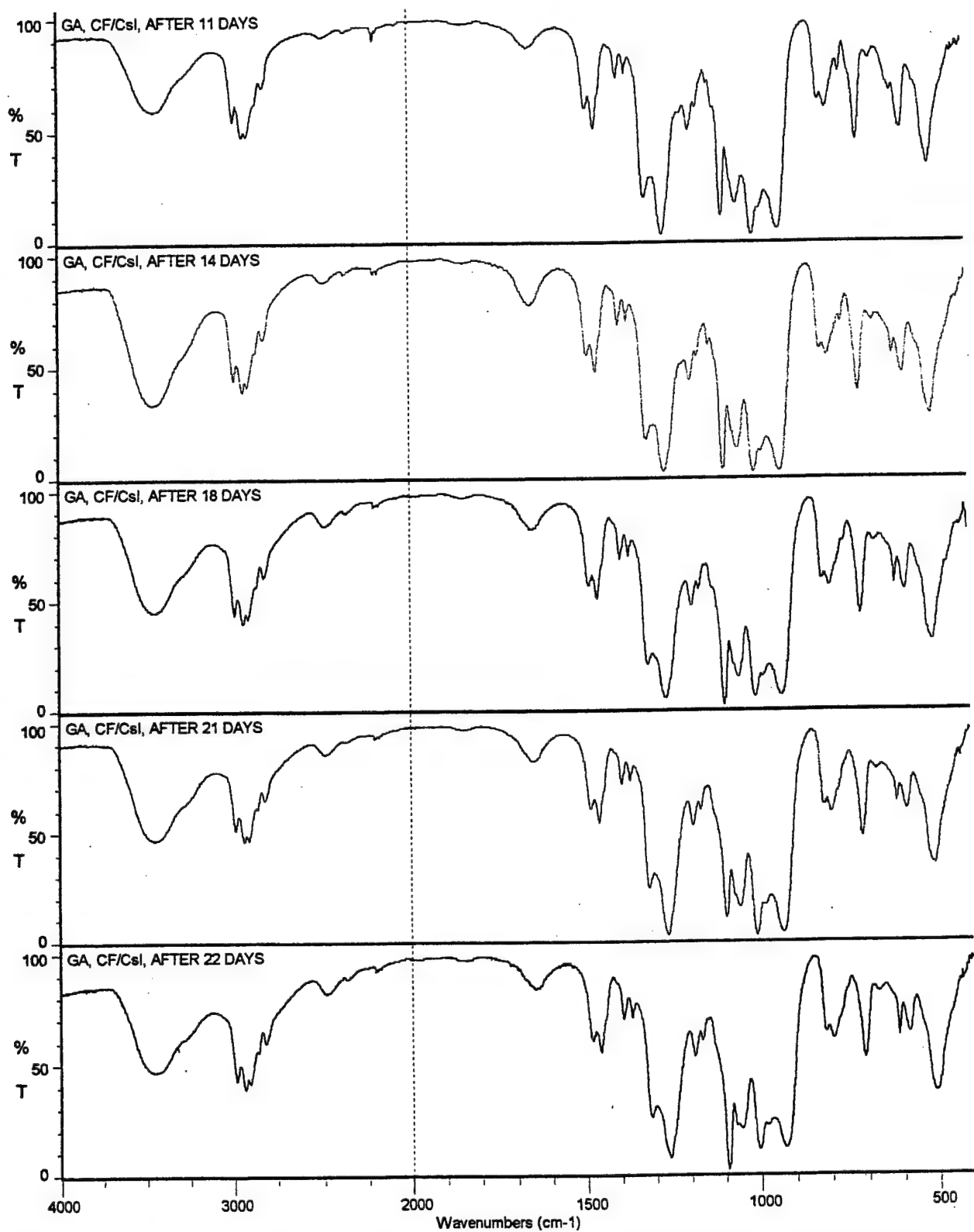


Figure 22 GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

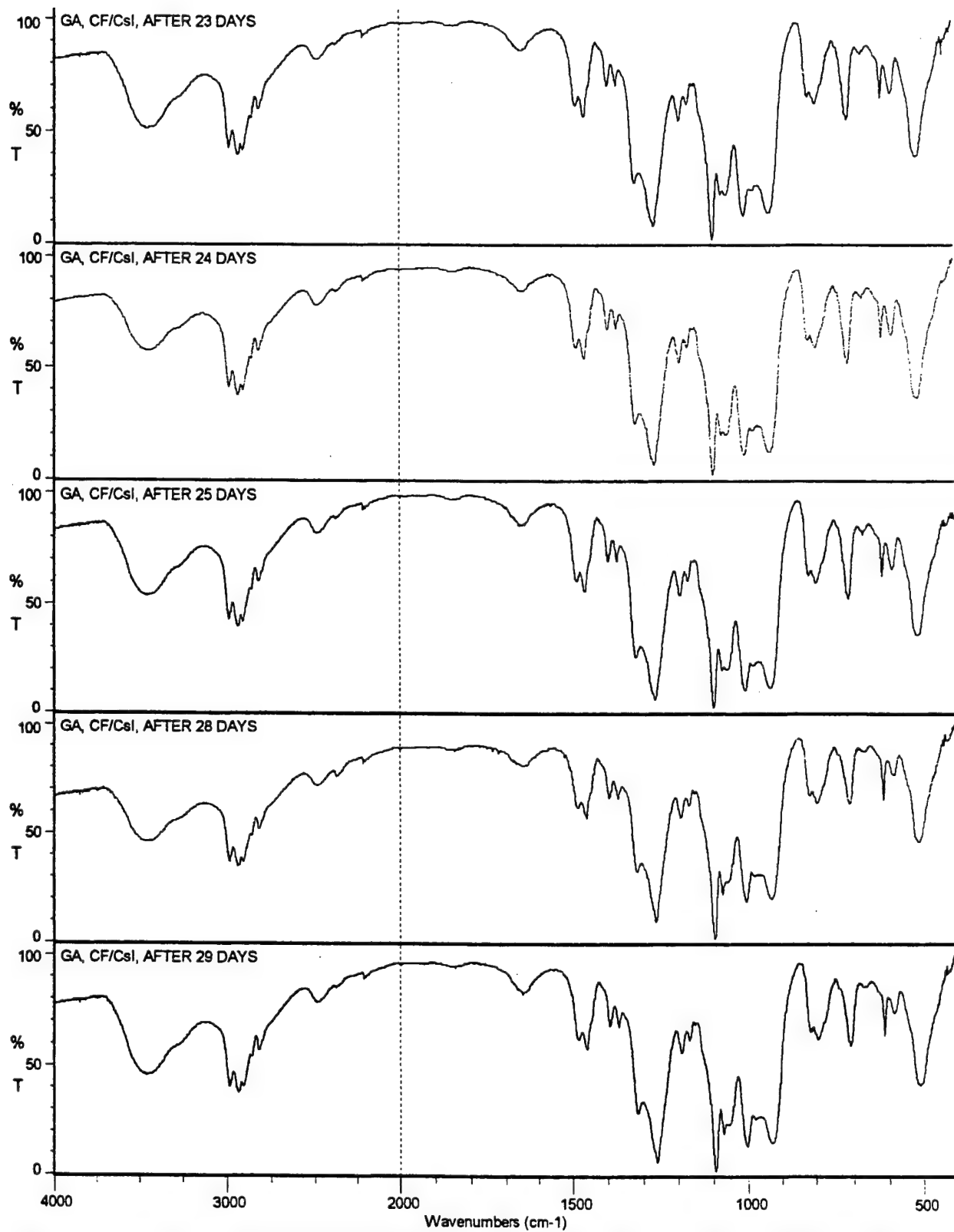


**Figure 22** GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

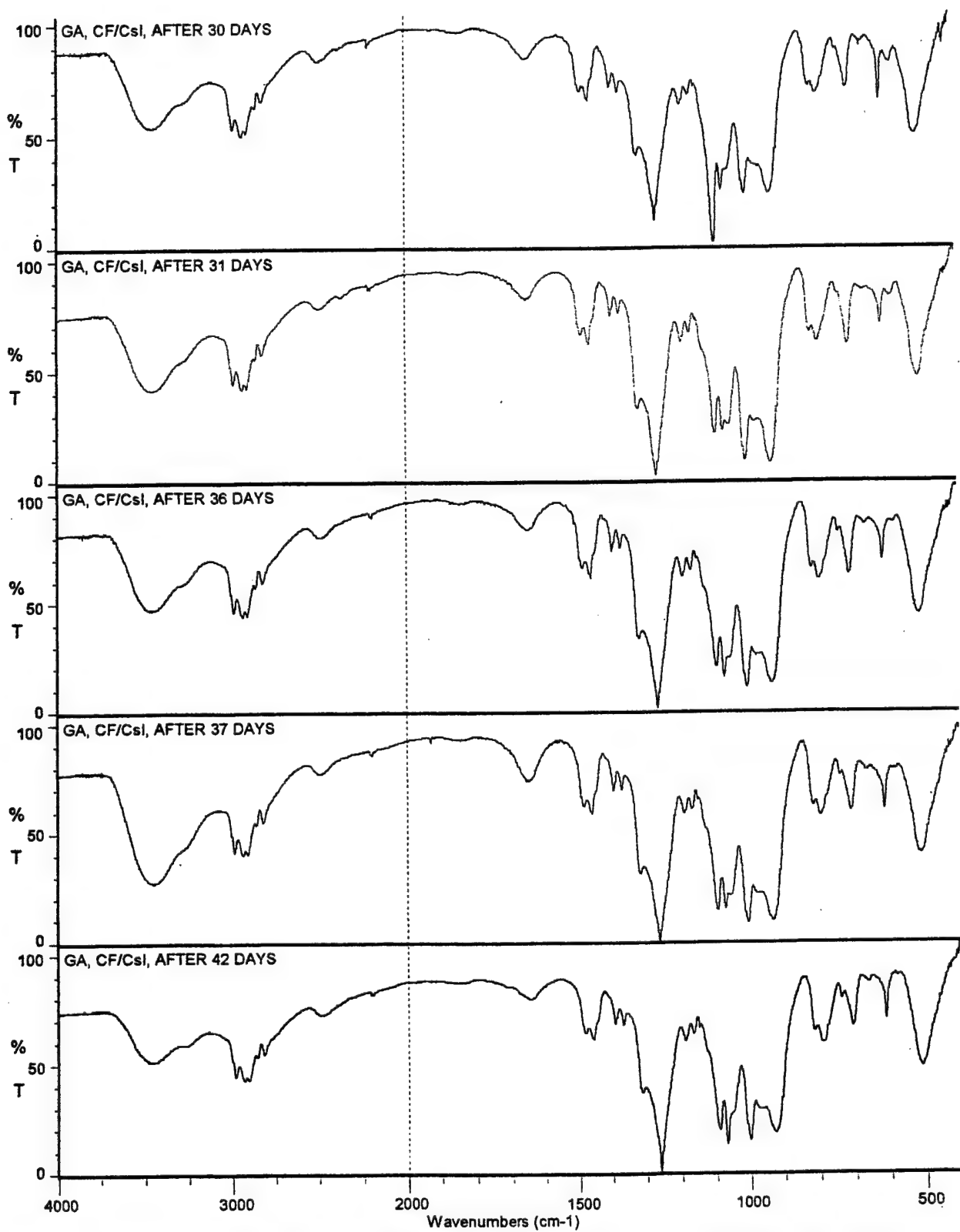




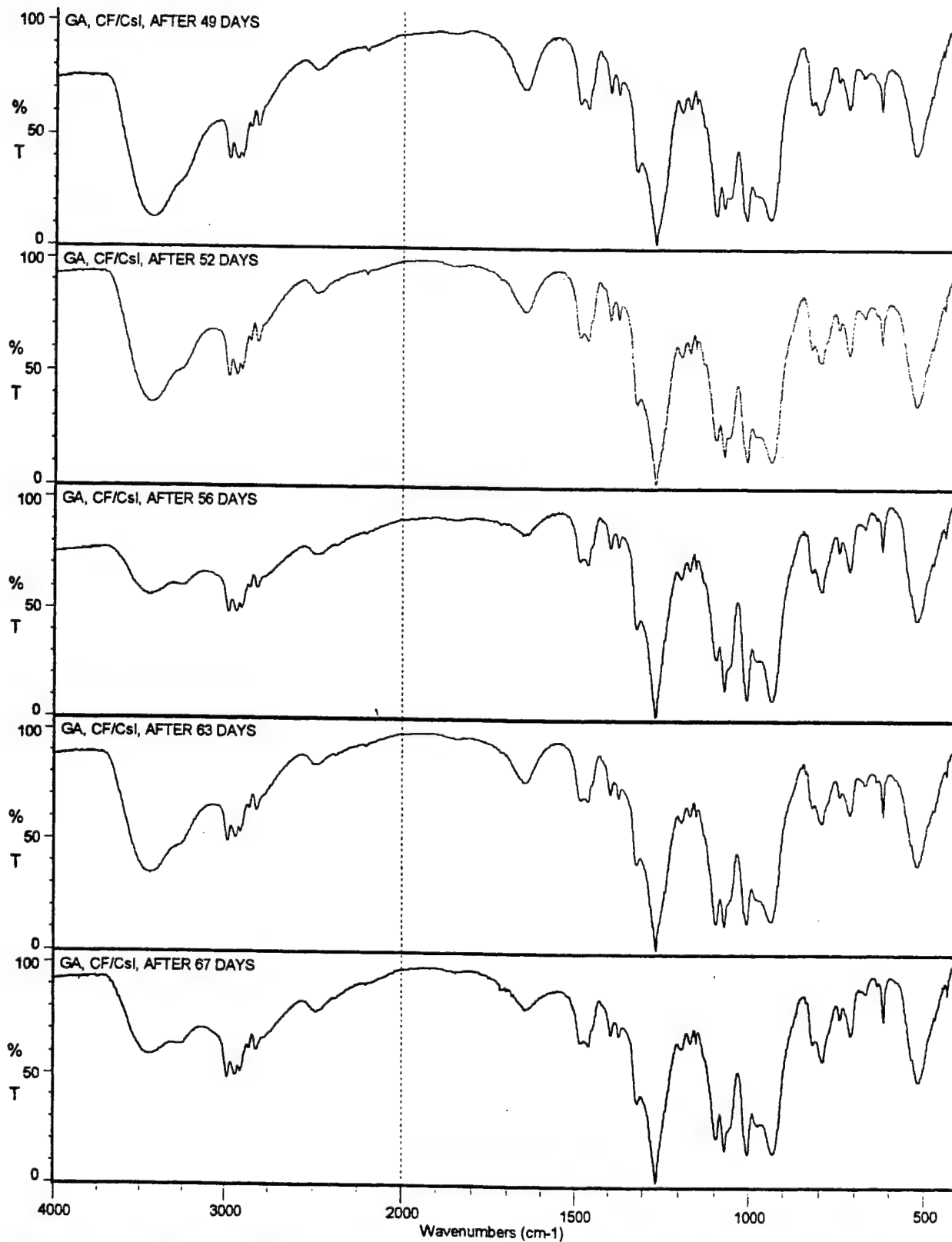
**Figure 22** GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)



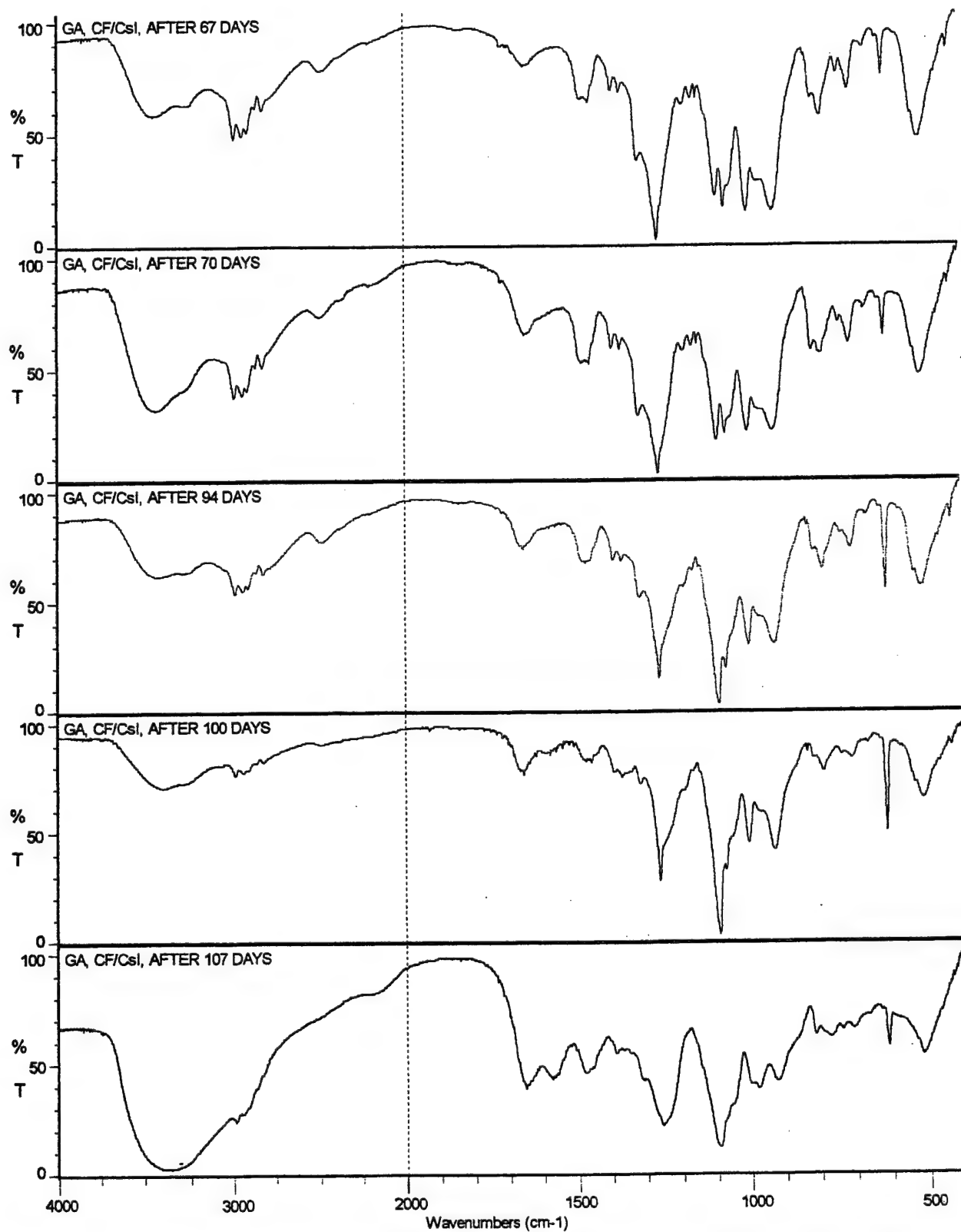
**Figure 22** GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)



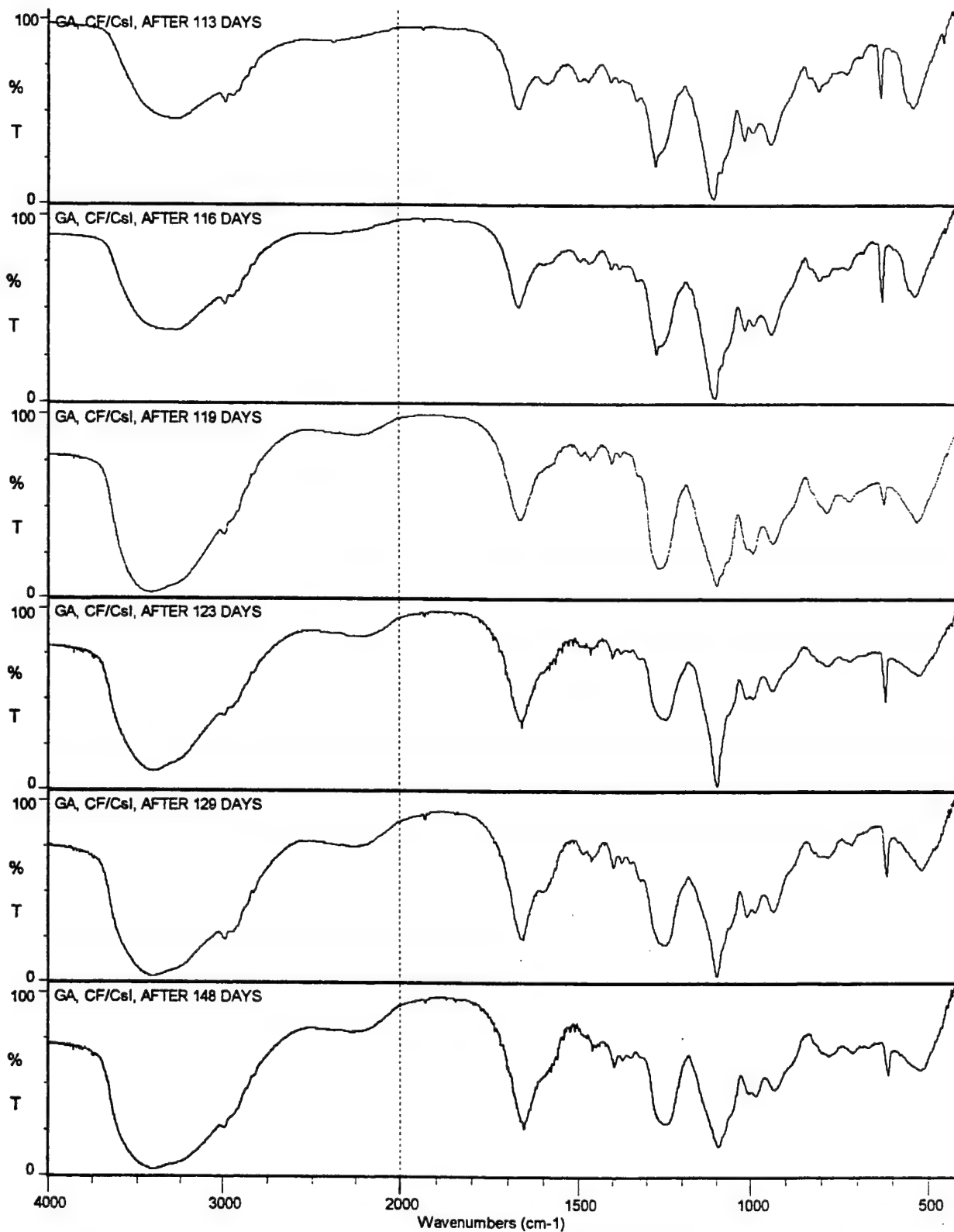
**Figure 22** GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)



**Figure 22** GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)



**Figure 22** GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)



**Figure 22** GA, ETHYL N,N-DIMETHYLPHOSPHORAMIDOCYANIDATE, 97.7%, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

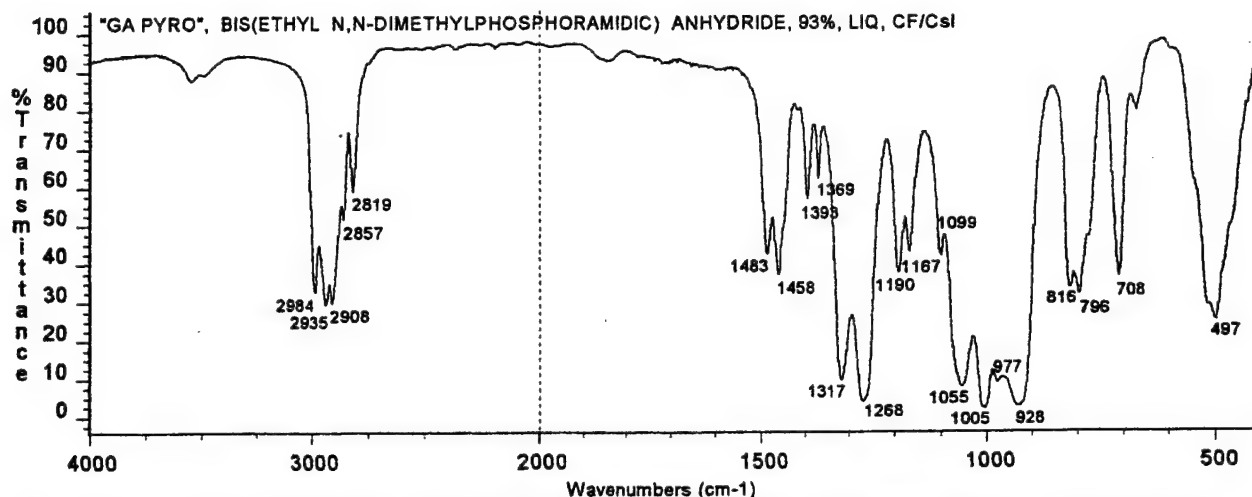


Figure 23 "GA PYRO", BIS(ETHYL N,N-DIMETHYLPHOSPHORAMIDIC ANHYDRIDE, 93%, LIQUID, CF/CsI

2984  $\text{cm}^{-1}$  m, 2935  $\text{cm}^{-1}$  m, 2908  $\text{cm}^{-1}$  m, 2857  $\text{cm}^{-1}$  w and 2819  $\text{cm}^{-1}$  w ( $\nu$   $\text{CH}_3$  and  $\text{CH}_2$ ), 1483  $\text{cm}^{-1}$  m ( $\delta$   $\text{OCH}_2$ ), 1458  $\text{cm}^{-1}$  m ( $\delta$   $\text{CH}_3$ ), 1393  $\text{cm}^{-1}$  w ( $\omega$   $\text{OCH}_2$ ), 1369  $\text{cm}^{-1}$  w ( $\delta_{\text{sy}}$   $\text{CH}_3$ ), 1317  $\text{cm}^{-1}$  ms [ $\text{P-N}(\text{CH}_3)_2$ ], 1268  $\text{cm}^{-1}$  s ( $\nu$   $\text{P=O}$ ), 1190  $\text{cm}^{-1}$  m [ $\text{P-N}(\text{CH}_3)_2$ ], 1167  $\text{cm}^{-1}$  w and 1099  $\text{cm}^{-1}$  w (characteristic of POEt,  $\text{CH}_3$  rock), 1055  $\text{cm}^{-1}$  ms ( $\nu$   $\text{P-O-C}$ ), 1005  $\text{cm}^{-1}$  s ( $\nu$   $\text{P-N-C}$ ), 977  $\text{cm}^{-1}$  vw ( $\nu$   $\text{C-C}$  of POEt), 928  $\text{cm}^{-1}$  s ( $\nu$   $\text{P-O-P}$  pyro moiety), 816  $\text{cm}^{-1}$  m, 796  $\text{cm}^{-1}$  m (POC), 708 m (PNC), 497  $\text{cm}^{-1}$  m ( $\delta$   $\text{P=O}$  ?).

Figure 24 shows the effect of atmospheric moisture on the infrared spectrum of GA PYRO. The compound remains intact in excess of 154 days. At the 175 day mark there is some decrease in the intensities of the bands indicative of the  $\text{PN}(\text{CH}_3)_2$  moiety (namely 1317, 1190, 1005 and 708  $\text{cm}^{-1}$ ). This decrease continues through the remainder of the observations until the last being at 212 days. After 212 days, some very weak absorption due to the  $\text{PN}(\text{CH}_3)_2$  moiety is still visible at 1316, 1009 and 709  $\text{cm}^{-1}$ . Bands are present at 1250  $\text{cm}^{-1}$  ( $\nu$   $\text{P=O}$ ), 1165  $\text{cm}^{-1}$  vw (POEt), 1056  $\text{cm}^{-1}$  s ( $\nu$   $\text{P-O-C}$ ), 969  $\text{cm}^{-1}$  sh ( $\nu$   $\text{C-C}$  of POEt), 923  $\text{cm}^{-1}$  ms ( $\nu$   $\text{P-O-P}$ ), 795  $\text{cm}^{-1}$  w (POC). Bands at 1090  $\text{cm}^{-1}$  s and 610  $\text{cm}^{-1}$  w are probably due to  $\text{Cs}_2\text{SO}_4$  from the CsI windows. Perhaps, another pyro compound such as  $(\text{HO})(\text{OEt})\text{P(=O)}-\text{O}-\text{P=O}(\text{OH})(\text{OEt})$  is being formed? The phosphoryl stretch of such a compound could occur near 1250  $\text{cm}^{-1}$  (see the reference given in footnote\* ).

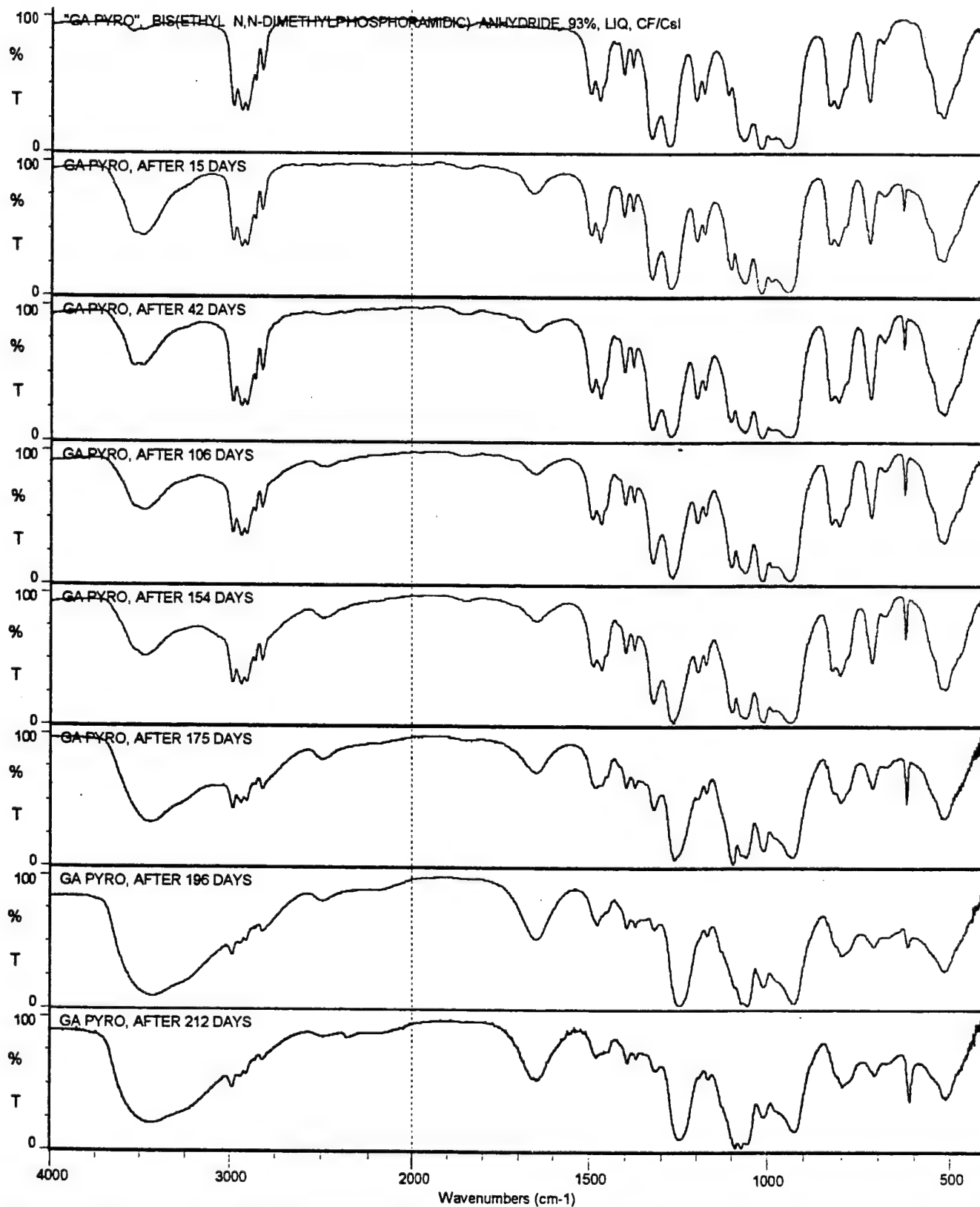


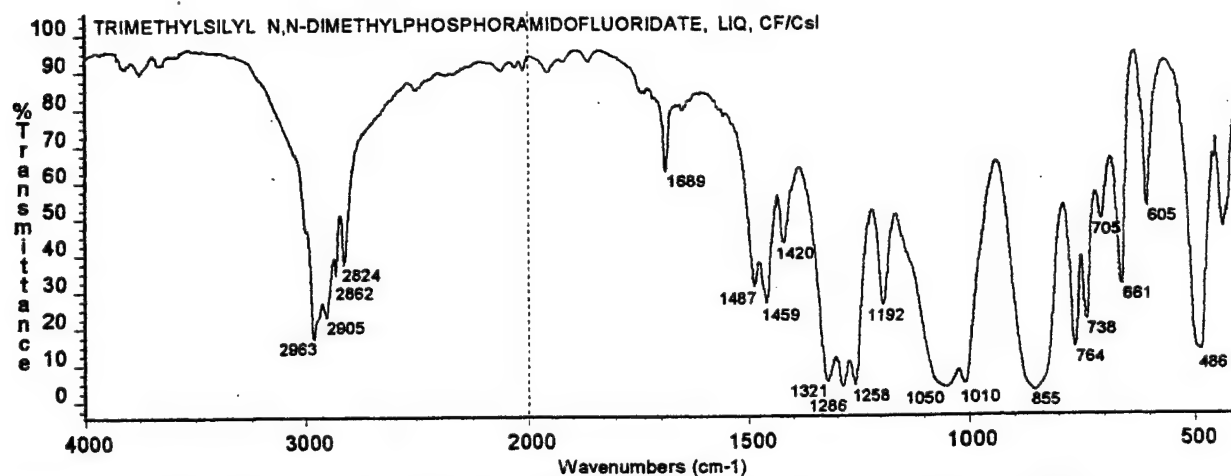
Figure 24 EFFECT OF ATMOSPHERIC MOISTURE ON GA PYRO, LIQUID, CF/CsI



### 3.1.10 Trimethylsilyl N,N-Dimethylphosphoramidofluoridate

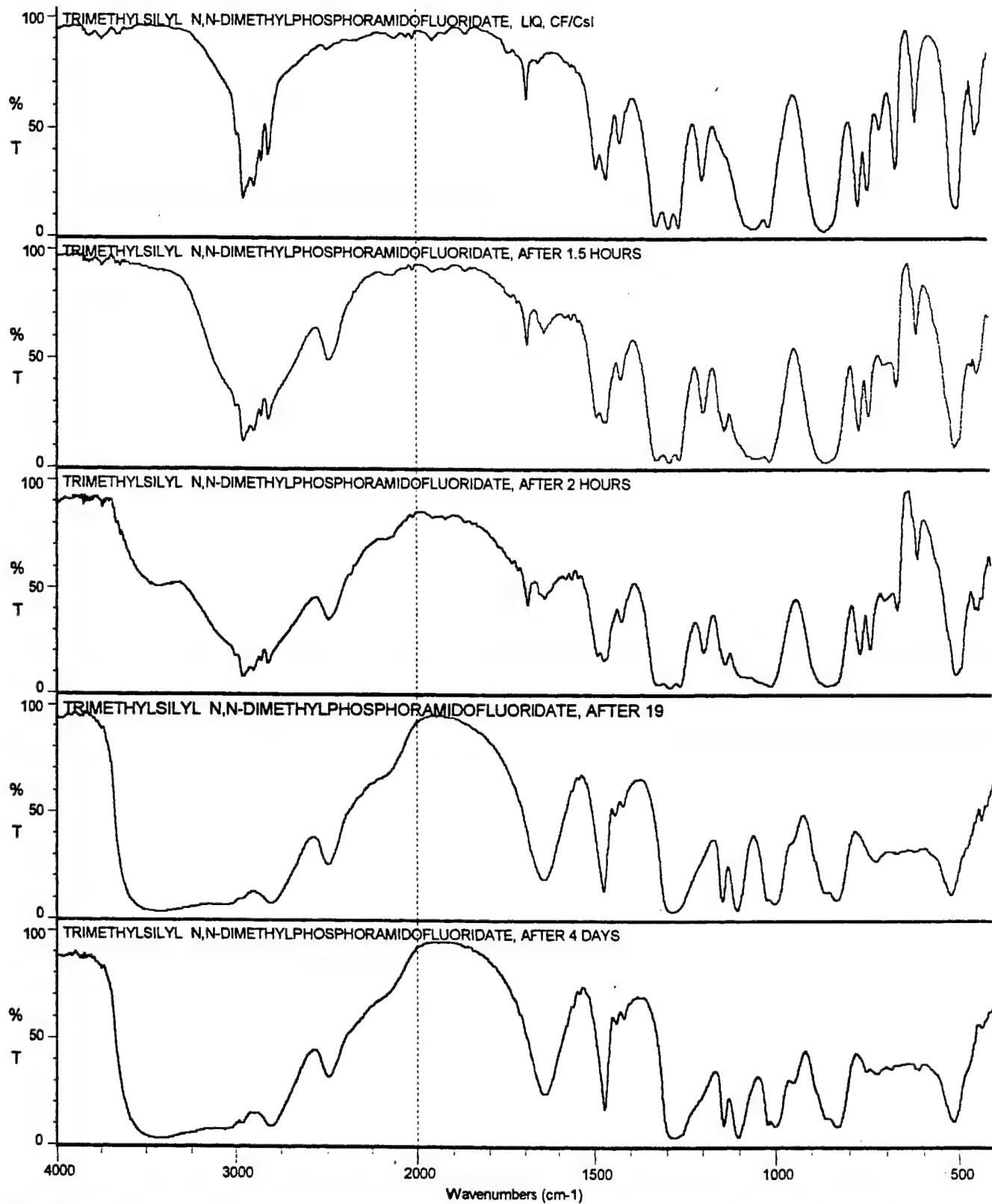


The infrared spectrum of trimethylsilyl N,N-dimethylphosphoramidofluoridate is given in *Figure 25*. The band assignments are as follows: 2963  $\text{cm}^{-1}$  ms, 2905  $\text{cm}^{-1}$  ms, 2862  $\text{cm}^{-1}$  m and 2824  $\text{cm}^{-1}$  m ( $\nu$  CH), 1689  $\text{cm}^{-1}$  w (The 855  $\text{cm}^{-1}$  band is believed to be composed of two bands with contributions from both the  $\text{Si}(\text{CH}_3)_3$  and  $\nu$  P-F, ca. 859 and 830  $\text{cm}^{-1}$ . The sum of these two bands would be ca. 1689  $\text{cm}^{-1}$ ), 1487  $\text{cm}^{-1}$  m and 1459  $\text{cm}^{-1}$  m ( $\delta$  CH<sub>3</sub>), 1420  $\text{cm}^{-1}$  w ( $\delta_{\text{as}}$  SiCH<sub>3</sub>), 1321  $\text{cm}^{-1}$  s [ $\text{PN}(\text{CH}_3)_2$ ], 1286  $\text{cm}^{-1}$  s ( $\nu$  P=O, the calculated value for the  $\nu$  P=O is 1302  $\text{cm}^{-1}$ . The average of 1321  $\text{cm}^{-1}$  and 1286  $\text{cm}^{-1}$  is 1304  $\text{cm}^{-1}$ ), 1258  $\text{cm}^{-1}$  s ( $\delta_{\text{sy}}$  SiCH<sub>3</sub>), 1192  $\text{cm}^{-1}$  w [ $\text{PN}(\text{CH}_3)_2$ ], 1050  $\text{cm}^{-1}$  s ( $\nu$  P-O-C), 1010  $\text{cm}^{-1}$  s ( $\nu$  P-N-C), 855  $\text{cm}^{-1}$  s (probably-contribution from both the SiCH<sub>3</sub> rock and  $\nu$  P-F), 764  $\text{cm}^{-1}$  m [ $\text{Si}(\text{CH}_3)_2$ ], 738  $\text{cm}^{-1}$  or 661  $\text{cm}^{-1}$  m [ $\text{PN}(\text{CH}_3)_2$ ], 486  $\text{cm}^{-1}$  ms ( $\delta$  P=O ?).

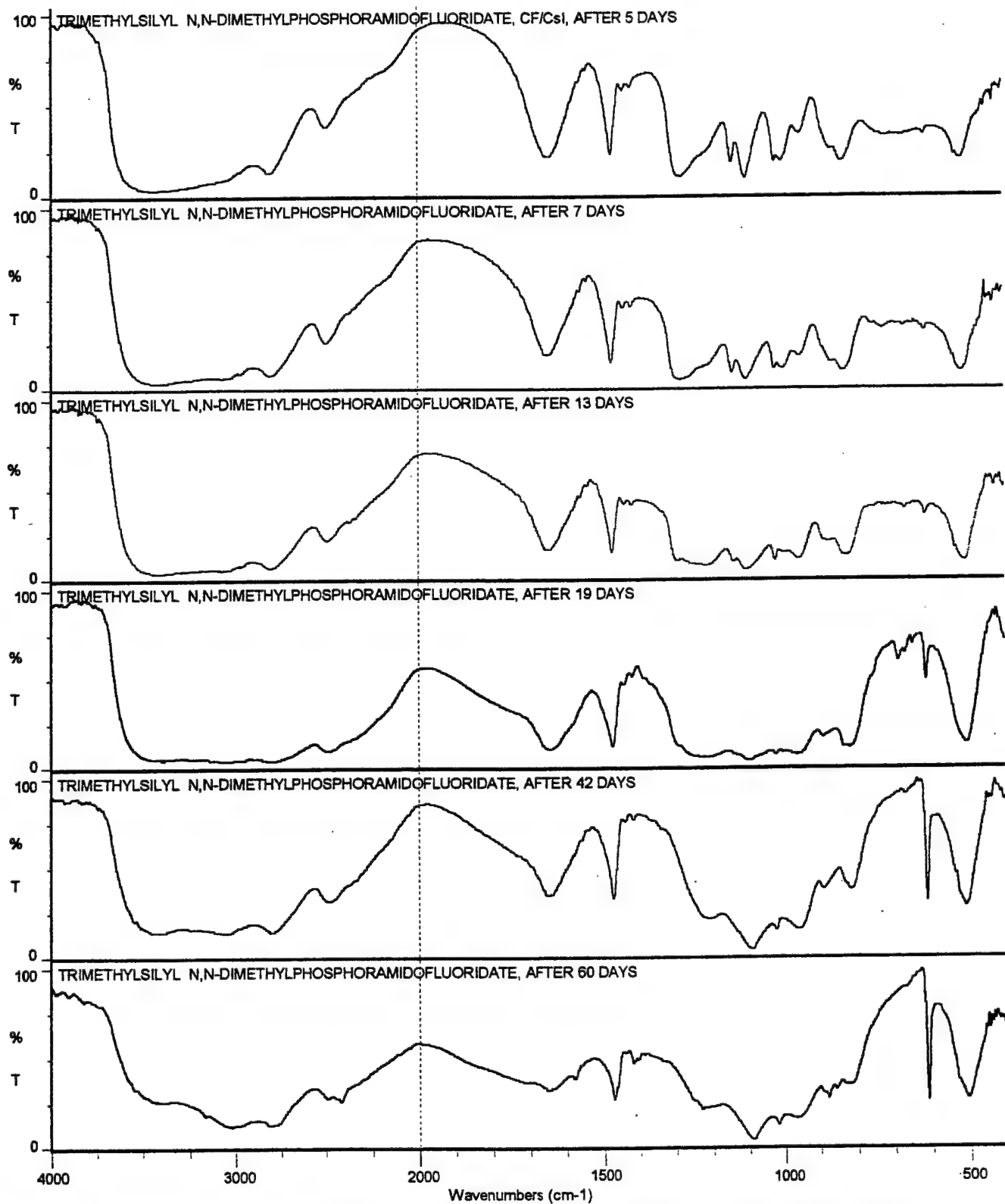


**Figure 25A** TRIMETHYLSILYL N,N-DIMETHYLPHOSPHORAMIDOFLUORIDATE, LIQUID, CF/CsI

The effect of atmospheric moisture on trimethylsilyl N,N-dimethylphosphoramidofluoridate is demonstrated in *Figures 25A & B*. Even as soon as 1.5 hours changes are apparent in the infrared spectrum as evidenced by the new band near 2500  $\text{cm}^{-1}$  and the broadening in the 3000  $\text{cm}^{-1}$  region. After 19 hours dramatic changes are apparent, namely bands near 3070, 2800 and 2500  $\text{cm}^{-1}$  ( $\text{NH}_2^+$ ), 1281 and 1103  $\text{cm}^{-1}$  which may be assigned to the asymmetric and symmetric stretching of the  $\text{PO}_2^-$  group. Bands due to the  $\text{PN}(\text{CH}_3)_2$  (1321, 1192, 1010, 738 or 661  $\text{cm}^{-1}$ ) are now absent from the spectrum. The



**Figure 25B** TRIMETHYLSILYL N,N-DIMETHYLPHOSPHORAMIDOFLUORIDATE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE



**Figure 25B** TRIMETHYLSILYL N,N-DIMETHYLPHOSPHORAMIDOFLUORIDATE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

Si(CH<sub>3</sub>)<sub>3</sub> group is still apparently present as the 1281 cm<sup>-1</sup> may be partly due to this moiety. The bands at 859 and 830 cm<sup>-1</sup> may still be due to the Si(CH<sub>3</sub>)<sub>3</sub> and the P-F moieties. The band at 1000 cm<sup>-1</sup> may be due to the P-OH group. The following compound may now be the prevalent species,

[HO-P(O<sub>2</sub>)F]<sup>-</sup> H<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub><sup>+</sup>. The final compound after 42-60 days may result from the removal of the fluorine to give [HOP(O<sub>2</sub>)OH]<sup>-</sup> H<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub><sup>+</sup>. This is indicated by the drop in the ν<sub>as</sub> PO<sub>2</sub><sup>-</sup> from 1281 to 1209 cm<sup>-1</sup> and the disappearance of the ν P-F band near 830 cm<sup>-1</sup>. Also present during the 42-60 day period are bands at 1091 and 611 cm<sup>-1</sup> which are believed to be due to the formation of Cs<sub>2</sub>SO<sub>4</sub> from the cesium iodide windows.

### 3.2 Precursors of G-Agents

Methylphosphonous dichloride, **SW** CAS [676-83-5]

Phosphorus trichloride, **TH** CAS [7719-12-2]

Methylphosphonic chlorofluoride

Methylphosphonic dichloride, **DC, Dichlor** CAS [676-97-1]

Methyl methylphosphinate

Dimethyl phosphite CAS [868-85-9]

Trimethyl phosphite, **TMP** CAS [121-45-9]

Dimethyl methylphosphonate, **DMMP** CAS [756-79-6]

Hydrogen methyl methylphosphonate (methyl methylphosphonic acid)

Diisopropyl phosphite CAS [1809-20-7]

Triisopropyl phosphite CAS [116-17-6]

3,3-Dimethylbutanone-2 (pinacolone) CAS [75-97-8]

#### 3.2.1 Methylphosphonous Dichloride (dichloromethylphosphine) SW CH<sub>3</sub>P(Cl)<sub>2</sub>

The infrared spectrum of methylphosphonous dichloride (**SW**), CH<sub>3</sub>P(Cl)<sub>2</sub>, is give in *Figure 26*.

The band assignments are as follows: 2992 cm<sup>-1</sup> vvw, 2925 cm<sup>-1</sup> vvw, 2905 cm<sup>-1</sup> vvw (ν CH<sub>3</sub>), 1405 cm<sup>-1</sup>

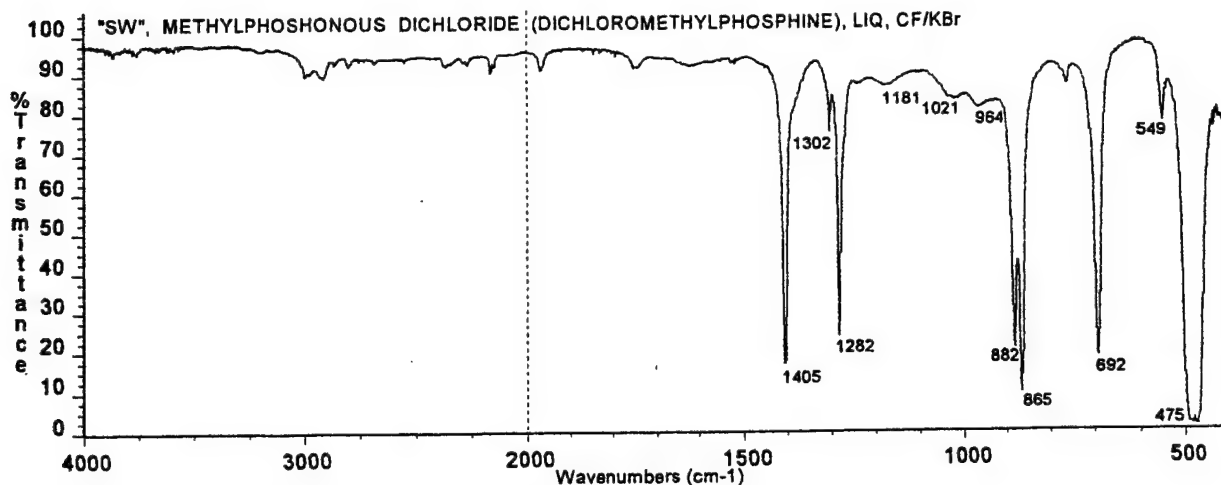


Figure 26 METHYLPHOSPHONOUS DICHLORIDE (SW), LIQUID, CF/KBr

m ( $\delta_{as}$  P-CH<sub>3</sub>), 1282 cm<sup>-1</sup> m  $\delta_{sy}$  P<sup>+3</sup>-CH<sub>3</sub> (a very weak band at 1302 cm<sup>-1</sup> is probably due to the  $\delta_{sy}$  P<sup>+5</sup>-CH<sub>3</sub>), 1181 cm<sup>-1</sup> vw broad  $\nu$  P=O of an acid, hydrolysis product. The bands at 1021 and 964 cm<sup>-1</sup> are also probably due to the  $\nu$  P-O(H) and the  $\nu$  P-O-P of a pyro moiety present as an impurity because of hydrolysis. The medium bands at 882 and 865 cm<sup>-1</sup> are due to the P-CH<sub>3</sub> rocking vibration. The medium band at 692 cm<sup>-1</sup> can be assigned to  $\nu$  P-C. The strong band at 475 cm<sup>-1</sup> is assigned to  $\nu$  PCl<sub>2</sub>.

The effect of atmospheric moisture on the spectrum of methylphosphonous dichloride is given in Figure 27. As time progressed to 75 minutes, the spectrum showed the following: ca 2750, 2250 and 1680 cm<sup>-1</sup> w broad (P-OH), ca 2430 cm<sup>-1</sup> vw ( $\nu$  P-H), 1405 vw cm<sup>-1</sup> ( $\delta_{as}$  P-CH<sub>3</sub>), 1308 cm<sup>-1</sup> w  $\delta_{sy}$  P<sup>+5</sup>CH<sub>3</sub> (the 1281 cm<sup>-1</sup>  $\delta_{sy}$  P<sup>+3</sup>-CH<sub>3</sub> band is decreasing in intensity), 1180 cm<sup>-1</sup> m ( $\nu$  P=O), 1015 cm<sup>-1</sup> s (P-H deformation), 961 cm<sup>-1</sup>  $\nu$  P-O(H), 882 cm<sup>-1</sup> w P-CH<sub>3</sub> rock and 691 cm<sup>-1</sup>  $\nu$  P-C. The band at 473 cm<sup>-1</sup> is decreasing in intensity and is assigned to the PCl<sub>2</sub> stretching vibration. As time passed the hydrolysis became more complete and the resultant spectrum resembled that of a phosphinic acid, namely methylphosphinic acid, CH<sub>3</sub>P=O(H)(OH). The sample of SW left exposed to atmospheric moisture overnight is somewhat wetter than the 105 minute sample and thus shows a lower  $\nu$  P=O (1180 to 1143 cm<sup>-1</sup>). Thus the hydrolysis of SW may be represented by: CH<sub>3</sub>PCl<sub>2</sub> + 2 HOH → CH<sub>3</sub>P=O(H)(OH) + 2HCl.

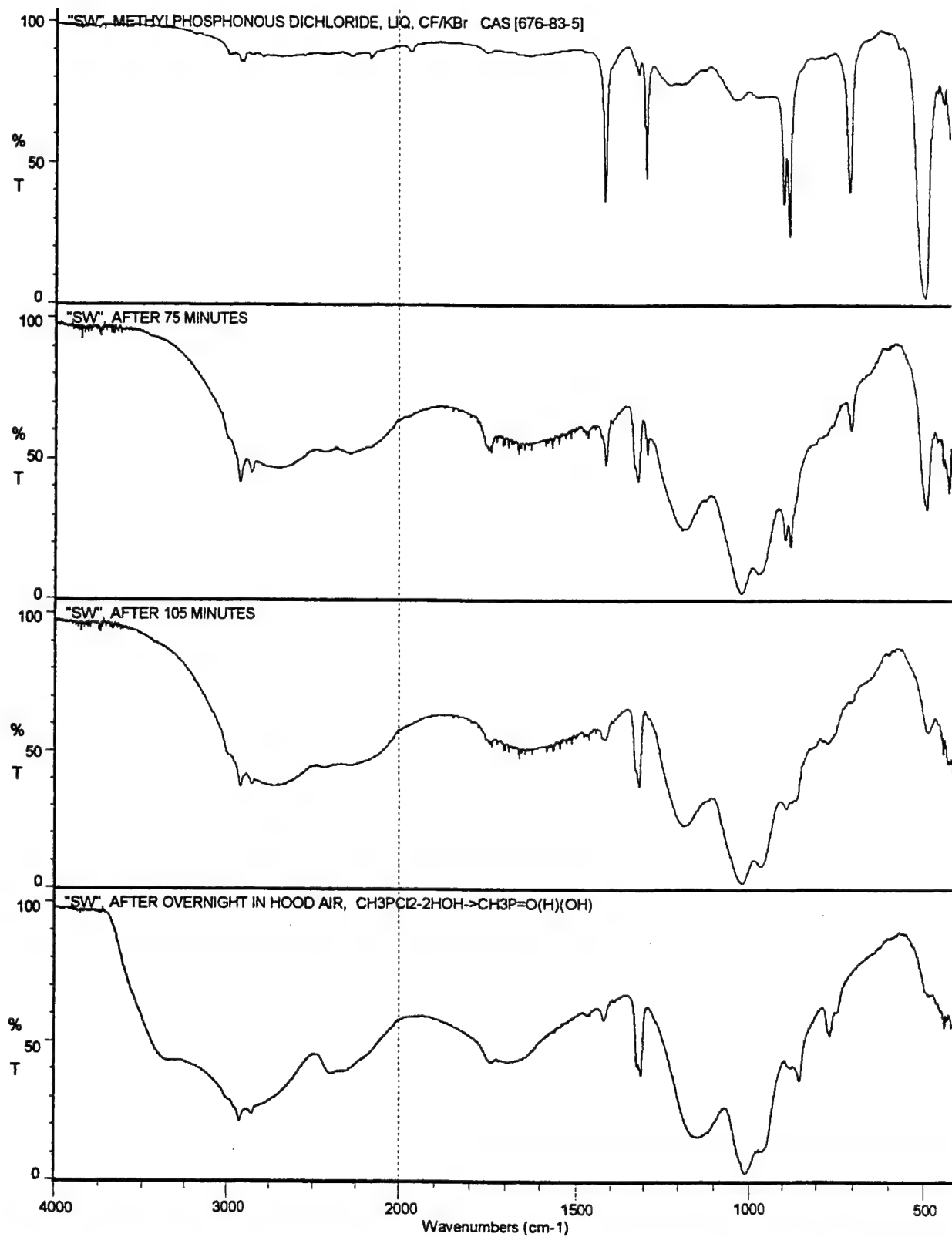


Figure 27 EFFECT OF ATMOSPHERIC MOISTURE ON METHYLPHOSPHONOUS DICHLORIDE (SW), LIQUID, CF/KBr

### 3.2.2 Methylphosphonic Dichloride (DC, Dichlor)

The infrared spectrum of methylphosphonic dichloride,  $\text{CH}_3\text{P}=\text{O}(\text{Cl})_2$ , is given in *Figure 28*.

The bands may be assigned as follows: 3005 and 2919  $\text{cm}^{-1}$  w ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$ ), 1405  $\text{cm}^{-1}$  w ( $\delta_{\text{as}}$   $\text{P}-\text{CH}_3$ ), 1384  $\text{cm}^{-1}$  vw ( $\text{KNO}_3$  from the KBr windows), 1305  $\text{cm}^{-1}$  m ( $\delta_{\text{sy}}$   $\text{P}-\text{CH}_3$ ), 1271  $\text{cm}^{-1}$  s ( $\nu \text{P}=\text{O}$ ), 968  $\text{cm}^{-1}$  vvw ( $\nu \text{P}-\text{OH}$  or  $\nu \text{P}-\text{O}-\text{P}$  ?), 895  $\text{cm}^{-1}$  m ( $\text{P}-\text{CH}_3$  rock), 764  $\text{cm}^{-1}$  m ( $\nu \text{P}-\text{C}$ ), 539  $\text{cm}^{-1}$  ms and 493  $\text{cm}^{-1}$  m ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{P}-\text{Cl}_2$ ).

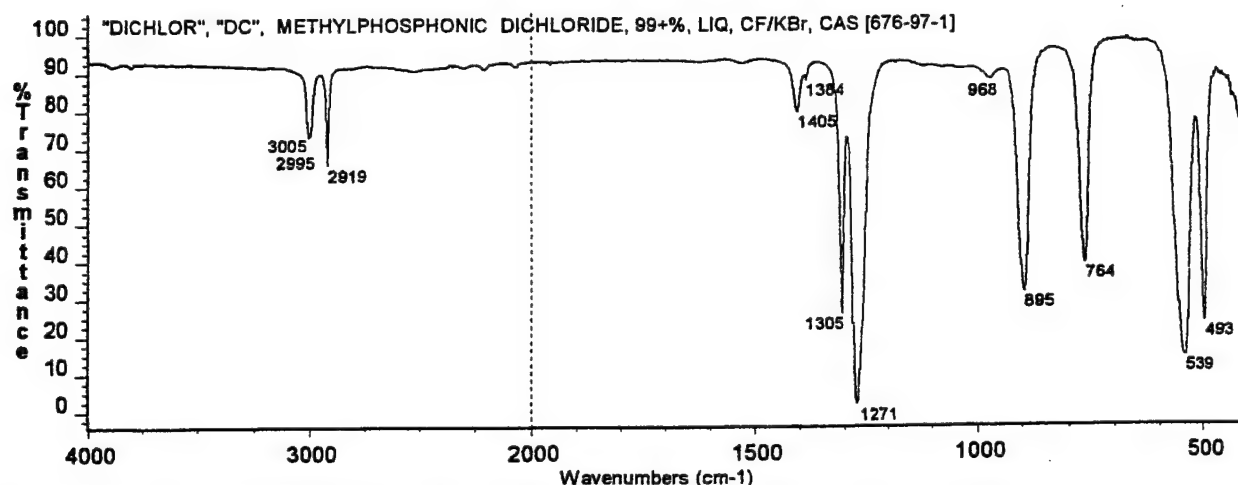


Figure 28 METHYLPHOSPHONIC DICHLORIDE (DICHLOR, DC), 99+%, LIQUID, CF/KBr

The effect of atmospheric moisture on the infrared spectrum of methylphosphonic dichloride is given in *Figure 29*. After an exposure of 22 hours to atmospheric moisture, the spectrum of Dichlor shows broad weak bands near 2800, 2340, 1650  $\text{cm}^{-1}$  and a strong band at 1008  $\text{cm}^{-1}$  due to the acid  $\text{POH}$  moiety. The  $\text{PCl}_2$  bands at 546 and 495  $\text{cm}^{-1}$  have become much weaker. The  $\text{P}=\text{O}$  stretching region shows multiple bands at 1270, 1256, 1242  $\text{cm}^{-1}$  and some broad diffuse absorption near 1150  $\text{cm}^{-1}$ . The first band 1270  $\text{cm}^{-1}$  being from the Dichlor, while the other bands may be due to methylphosphonic anhydride (a pyro compound) and methylphosphonic acid as well as other intermediates. The infrared spectra after 3 and 14 days show mainly the presence of a very wet methylphosphonic acid (MPA),  $\text{CH}_3\text{P}=\text{O}(\text{OH})_2$ . An infrared spectrum for a sample of water and MPA was reproduced earlier as *Figure 20*.

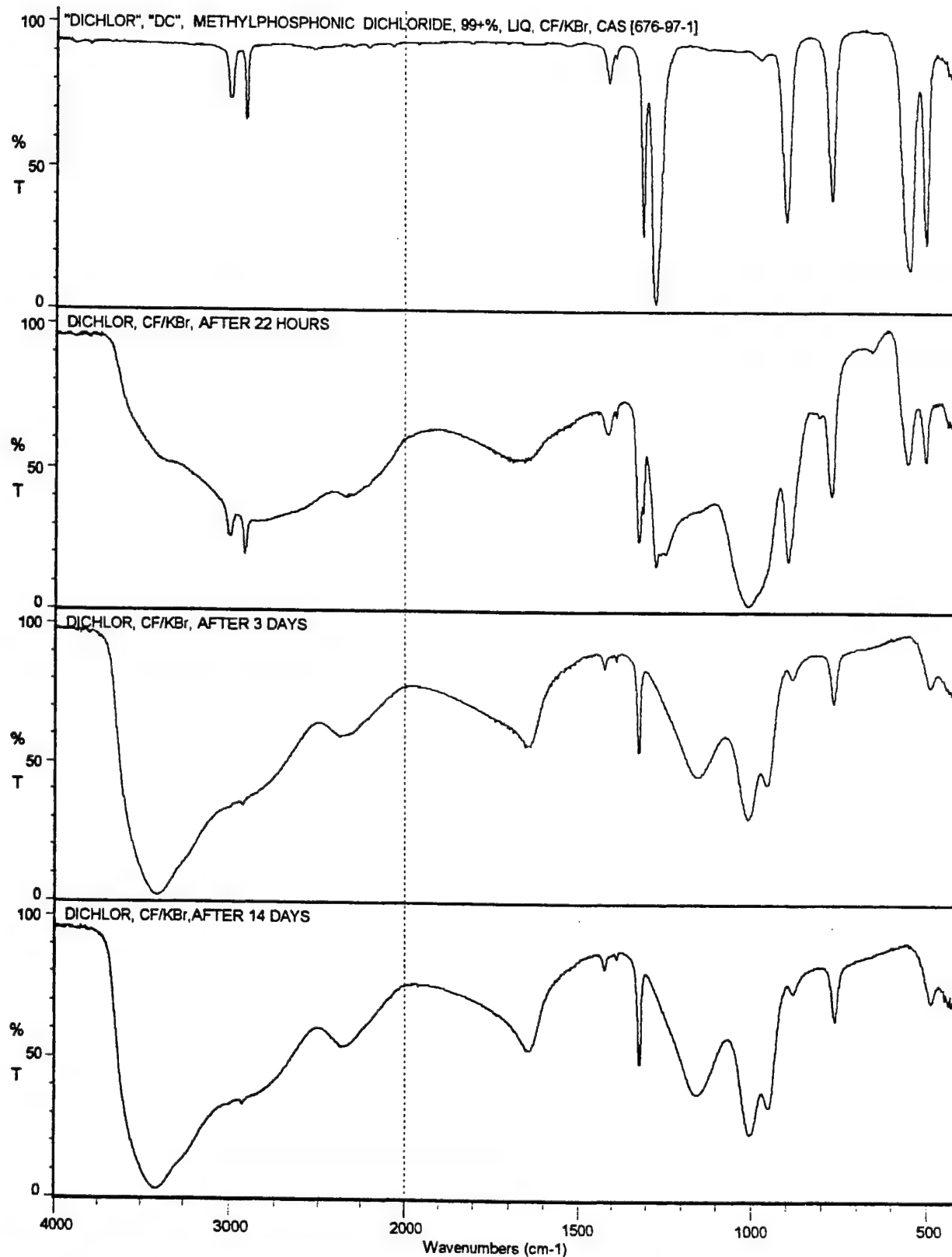
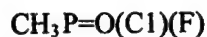


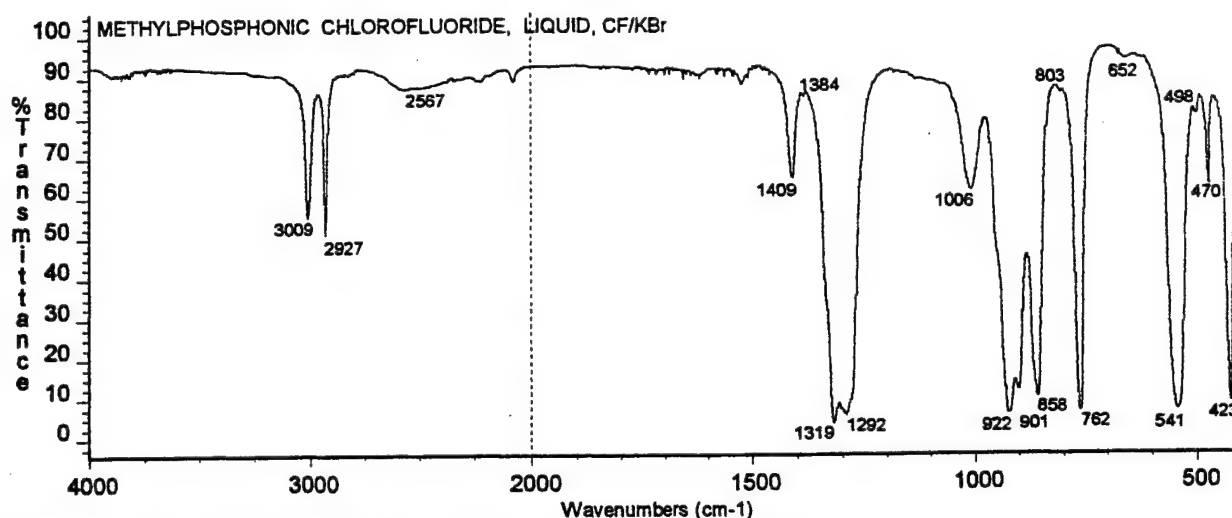
Figure 29 METHYLPHOSPHONIC DICHLORIDE, (DICHLOR, DC), LIQUID, CF/KBr, EXPOSED TO ATMOSPHERIC MOISTURE



### 3.2.3 Methylphosphonic Chlorofluoride

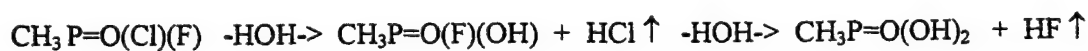


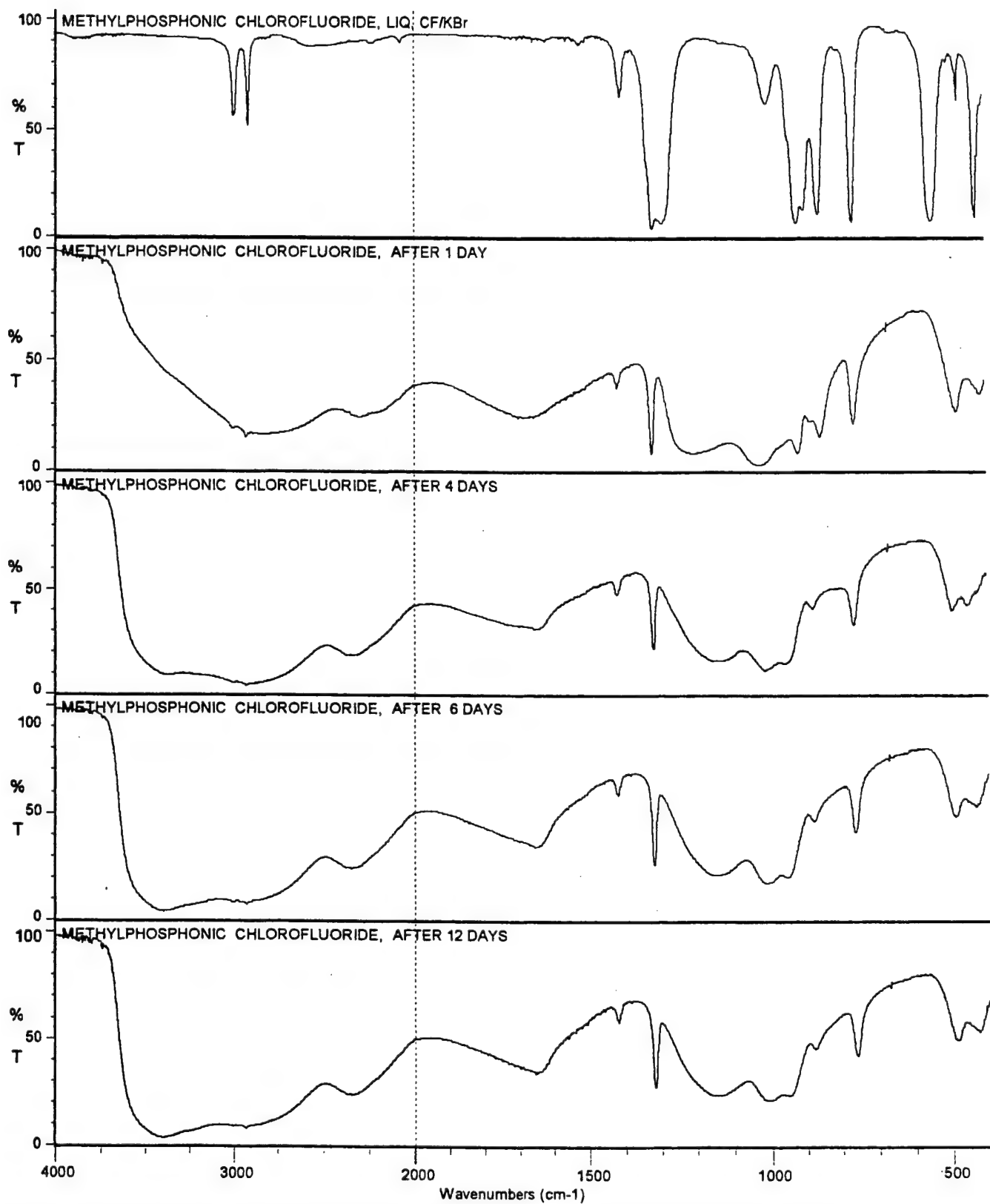
The infrared spectrum of methylphosphonic chlorofluoride,  $\text{CH}_3\text{P}=\text{O}(\text{Cl})(\text{F})$ , is reproduced in **Figure 30**. Band assignments are as follows: 3009 w and 2927  $\text{cm}^{-1}$  w ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$ ), 2567  $\text{cm}^{-1}$  vw broad (POH), 1409  $\text{cm}^{-1}$  w ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ), 1384  $\text{cm}^{-1}$  vvw ( $\text{KNO}_3$  from the KBr windows), 1319  $\text{cm}^{-1}$  s ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ), 1292  $\text{cm}^{-1}$  s ( $\nu$  P=O), 1006  $\text{cm}^{-1}$  w ( $\nu$  P-OH), ca 950  $\text{cm}^{-1}$  sh ( $\nu$  P-O-P pyro ?), 922  $\text{cm}^{-1}$  s and 901  $\text{cm}^{-1}$  ms (P- $\text{CH}_3$  antisymmetrical and symmetrical rocking respectively), 858  $\text{cm}^{-1}$  ms ( $\nu$  P-F), 762  $\text{cm}^{-1}$  s ( $\nu$  P-C), ca 655  $\text{cm}^{-1}$  vvw (pyro ?), 541  $\text{cm}^{-1}$  s ( $\nu$  P-Cl), 423  $\text{cm}^{-1}$  ms (P-F bending).



**Figure 30 METHYLPHOSPHONIC CHLOROFLUORIDE, LIQUID, CF/KBr**

The effect of atmospheric moisture on the infrared spectra of methylphosphonic chlorofluoride is given in **Figure 31**. After 1 day in moist air the liquid film showed mainly the Fluoro Acid, methylphosphonofluoridic acid,  $\text{CH}_3\text{P}=\text{O}(\text{F})(\text{OH})$ , with some residual  $\nu$  P-F still visible at 855  $\text{cm}^{-1}$ . Over the period of 4 to 12 days, the spectrum is mainly that of a very wet specimen of methylphosphonic acid (MPA),  $\text{CH}_3\text{P}=\text{O}(\text{OH})_2$ . This last spectrum (after 12 days) may be compared to **Figure 20** which is the infrared spectrum of an authentic but very wet sample of MPA. The hydrolysis of methylphosphonic chlorofluoride may be summarized as follows:



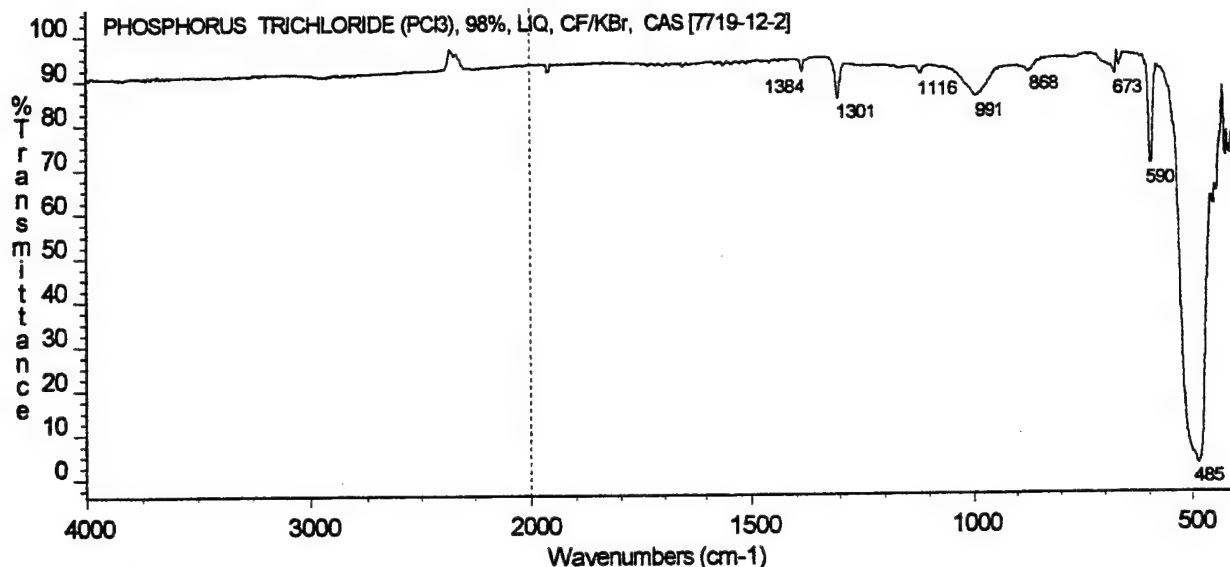


**Figure 31 EFFECT OF ATMOSPHERIC MOISTURE ON METHYLPHOSPHONIC CHLOROFLUORIDE, LIQUID, CF/KBr**

### 3.2.4 Phosphorus Trichloride (TH)



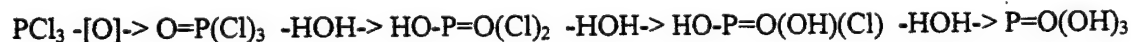
The infrared spectrum of phosphorus trichloride (TH) is reproduced in *Figure 32*. The infrared

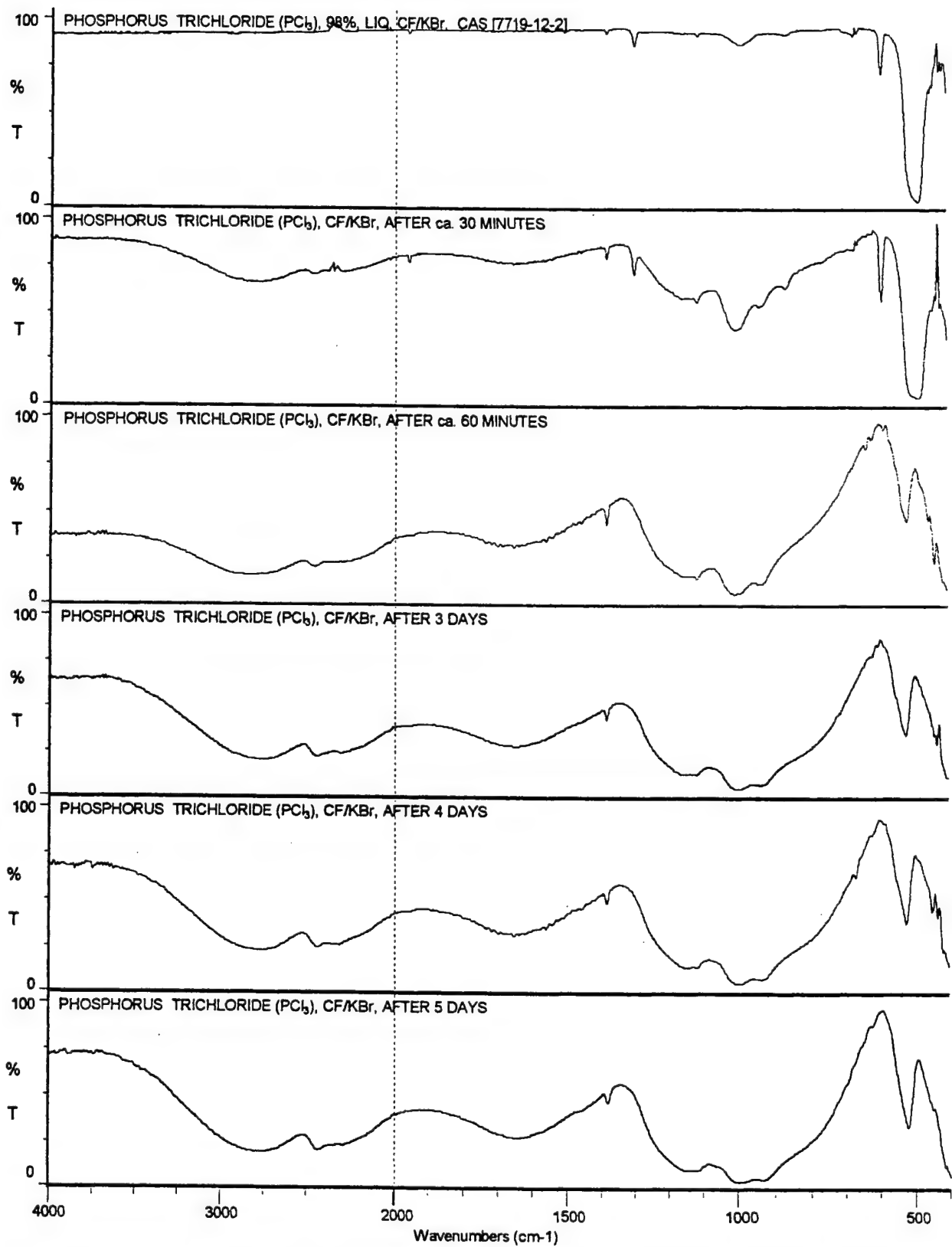


**Figure 32** PHOSPHORUS TRICHLORIDE (TH), 98%, LIQUID, CF/KBr

spectrum of phosphorus trichloride (TH) showed the following bands: 1384 cm<sup>-1</sup> (KNO<sub>3</sub> from the KBr windows), 1301 cm<sup>-1</sup> (ν P=O possibly from POCl<sub>3</sub>, which has a ν P=O of 1298 cm<sup>-1</sup>), 991 cm<sup>-1</sup> (ν P-OH ?), 485 cm<sup>-1</sup> (ν PCl<sub>3</sub>).

The effect of atmospheric moisture on the infrared spectrum of phosphorus trichloride (TH) is presented in *Figure 33*. After 30 minutes, the presence of a P-acid moiety is evident by the bands at 2799, 2451, ca 1650, 1159, 1005 and 937 cm<sup>-1</sup>. The 2451 cm<sup>-1</sup> band may also be due to the ν P-H of a compound such as H-P=O(OH)<sub>2</sub>, phosphorous acid (H<sub>3</sub>PO<sub>3</sub>). After 60 minutes the PCl<sub>3</sub> band, which was at 485 cm<sup>-1</sup>, is gone. The final product(s) after 5 days may be a combination of products such as H-P=O(OH)<sub>2</sub>, and HO-P=O(OH)<sub>2</sub>. The former compound arising from the hydrolysis of PCl<sub>3</sub>, while the latter compound (phosphoric acid, H<sub>3</sub>PO<sub>4</sub>) coming from the oxidation of PCl<sub>3</sub> followed by hydrolysis:



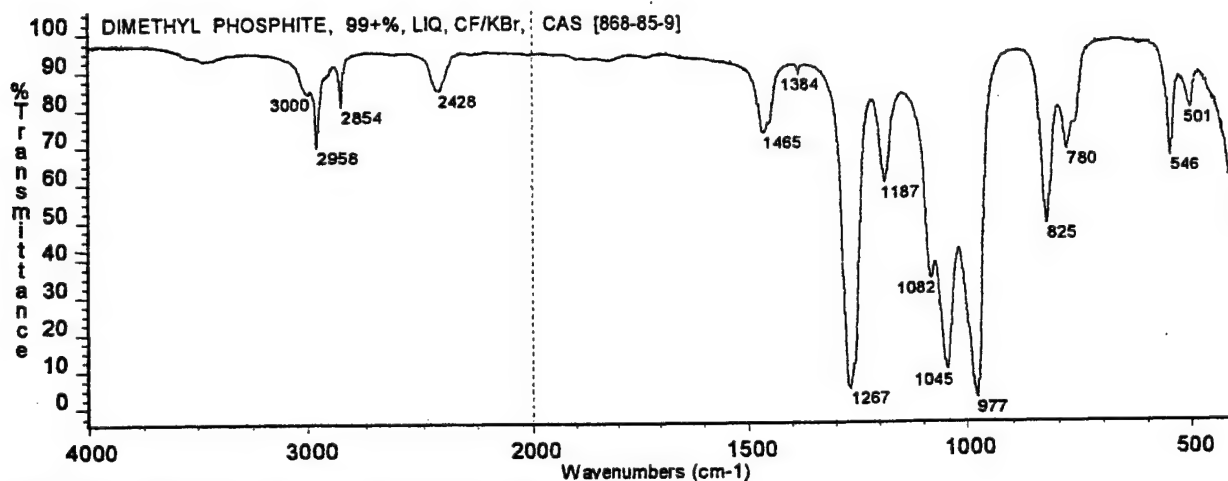


**Figure 33 EFFECT OF ATMOSPHERIC MOISTURE ON PHOSPHORUS TRICHLORIDE, LIQUID, CF/KBr**

### 3.2.5 Dimethyl Phosphite



The infrared spectrum of dimethyl phosphite,  $\text{H-P=O(OCH}_3)_2$ , is given in **Figure 34**. The band assignments are as follows:  $3000\text{ cm}^{-1}$  vw,  $2958\text{ cm}^{-1}$  w ( $\nu_{\text{as}} \text{CH}_3$ ),  $2854\text{ cm}^{-1}$  w ( $\nu_{\text{sy}} \text{CH}_3$ ),  $2428\text{ cm}^{-1}$  vw ( $\nu \text{ P-H}$ ),  $1465\text{ cm}^{-1}$  w ( $\delta \text{CH}_3$ ),  $1384\text{ cm}^{-1}$  vvw ( $\text{KNO}_3$  from the KBr windows),  $1267\text{ cm}^{-1}$  s ( $\nu \text{ P=O}$ ),  $1187\text{ cm}^{-1}$  w ( $\text{CH}_3$  rock, characteristic of  $\text{POCH}_3$ ),  $1082\text{ m}$  and  $1045\text{ cm}^{-1}$  ms ( $\nu \text{ P-O-C}$ ),  $977\text{ cm}^{-1}$  s (P-H deformation),  $825\text{ m}$  and  $780\text{ cm}^{-1}$  w (POC),  $546\text{ cm}^{-1}$  w (P=O deformation).



**Figure 34** DIMETHYL PHOSPHITE, 99+%, LIQUID, CF/KBr

The effect of environmental moisture of the infrared spectrum of dimethyl phosphite is illustrated in **Figure 35**. The infrared spectrum remains essentially the same up to the time of 44 hours of exposure to atmospheric moisture. New weak bands appear near  $3494$  and  $1650\text{ cm}^{-1}$  due to the adsorption of water by the compound. A dramatic change is visible in the infrared spectrum after 6 days have elapsed. Bands indicative of the P-acid moiety are evident near  $2800\text{ w}$ ,  $2300\text{ w}$ ,  $1650\text{ w}$ ,  $1010\text{ s}$  and  $939\text{ cm}^{-1}$  w (P-OH),  $2430\text{ cm}^{-1}$  w ( $\nu \text{ P-H}$ ),  $1150\text{ cm}^{-1}$  m ( $\nu \text{ P=O}$ ),  $525\text{ cm}^{-1}$  w (P=O deformation). No bands appear to be present from the  $\text{OCH}_3$  groups, as these appear to have been hydrolyzed off. The spectrum stays essentially the same up to the 41 day mark, with just a slight increase in the amount of adsorbed water. The final spectrum appears to be consistent with that expected for the compound, phosphorous acid,  $\text{P(OH)}_3$ , that is  $\text{H-P=O(OH)}_2$ .

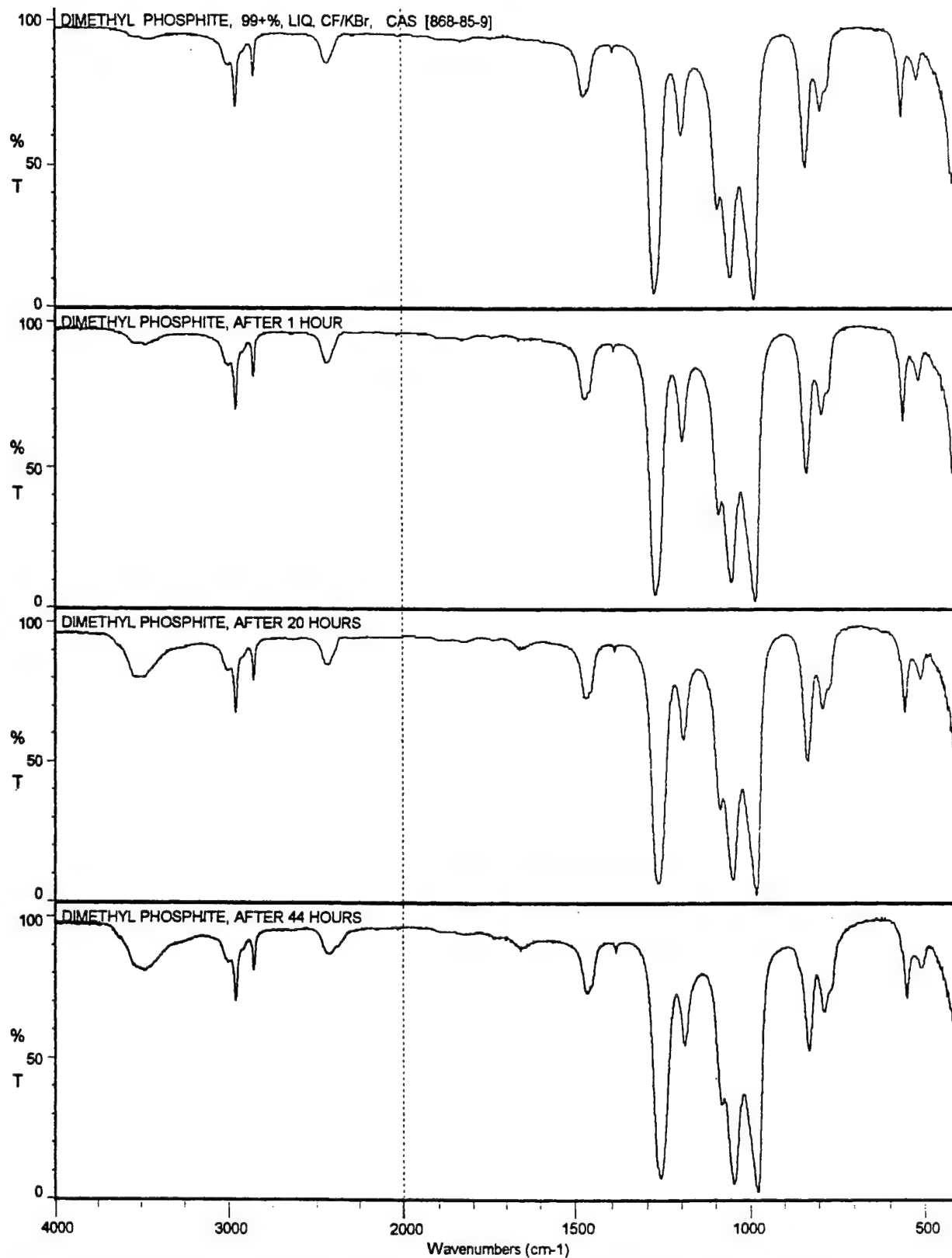
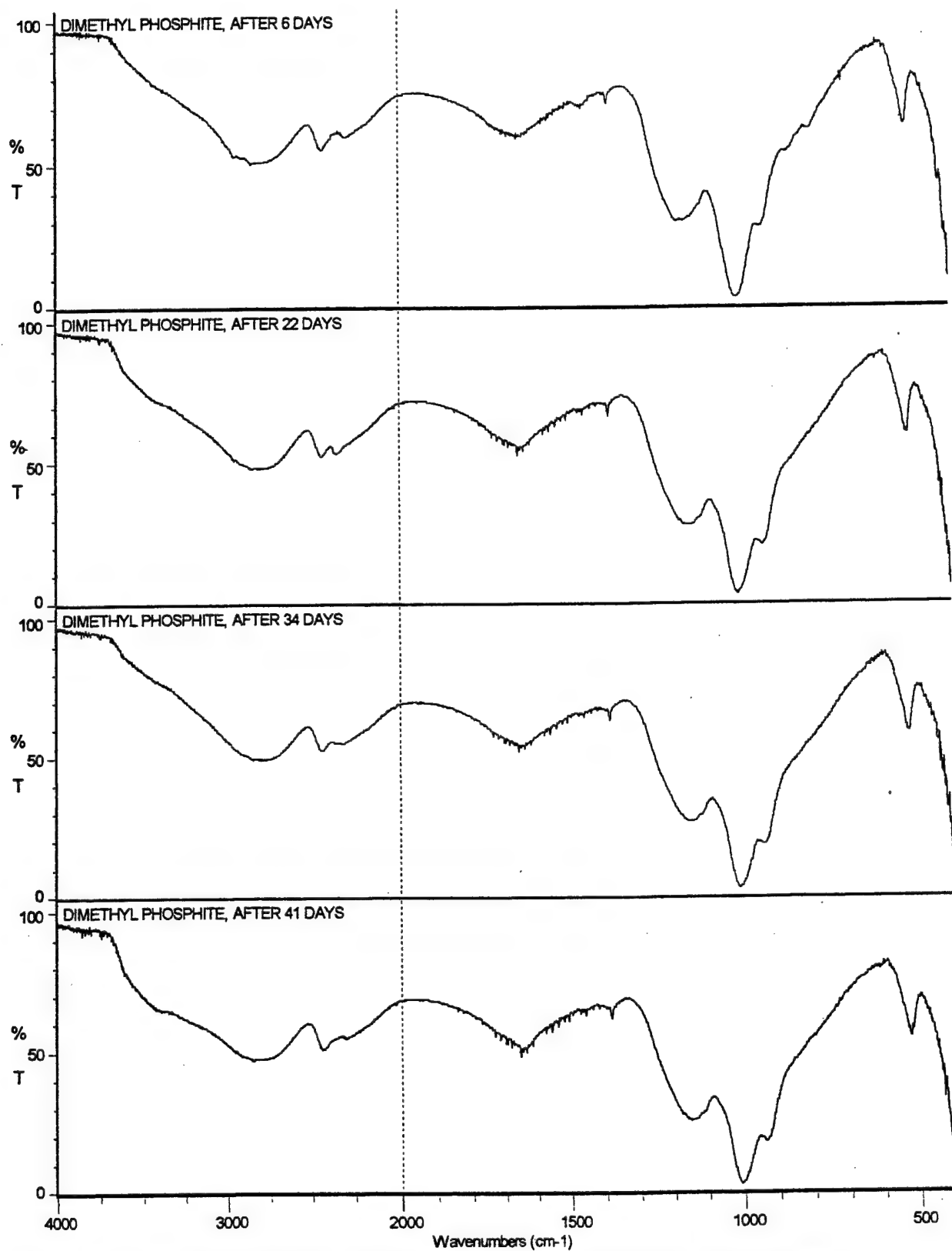


Figure 35 EFFECT OF ATMOSPHERIC MOISTURE ON DIMETHYL PHOSPHITE, LIQUID, CF/KBr



**Figure 35 EFFECT OF ATMOSPHERIC MOISTURE ON DIMETHYL PHOSPHITE, LIQUID, CF/KBr**  
(CONTINUED)

### 3.2.6 Trimethyl Phosphite (TMP)



The infrared spectrum of trimethyl phosphite (TMP) is reproduced in *Figure 36*. The band assignments are as follows: 2986  $\text{cm}^{-1}$  vw, 2946  $\text{cm}^{-1}$  w ( $\nu_{\text{as}}$   $\text{CH}_3$ ), 2836  $\text{cm}^{-1}$  w ( $\nu_{\text{sy}}$   $\text{CH}_3$ ), 1458  $\text{cm}^{-1}$  vw ( $\delta$   $\text{CH}_3$ ), 1384  $\text{cm}^{-1}$  vvw ( $\text{KNO}_3$  from the KBr windows), 1181  $\text{cm}^{-1}$  w ( $\text{CH}_3$  rock, characteristic of  $\text{POCH}_3$ ), 1057  $\text{cm}^{-1}$  sh and 1013  $\text{cm}^{-1}$  s ( $\nu$  P-O-C), 768  $\text{cm}^{-1}$  sh and 729  $\text{cm}^{-1}$  m (POC), 513  $\text{cm}^{-1}$  vw (POC).

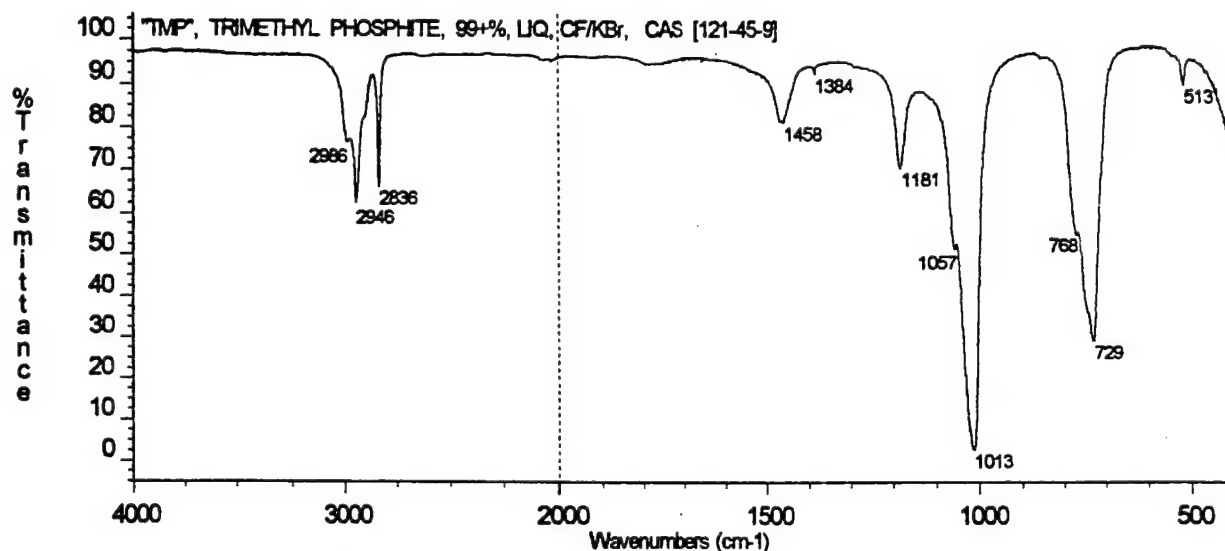


Figure 36 TRIMETHYL PHOSPHITE, 99+%, LIQUID, CF/KBr

The effect of the environment on the infrared spectrum of a film of liquid trimethyl phosphite between KBr windows is presented in *Figure 37*. After 2.5 hours the liquid film shows the beginnings of a band near 1280  $\text{cm}^{-1}$  and one near 852  $\text{cm}^{-1}$ . These are due to a  $\nu$  P=O and a POC vibration respectively. The  $\text{P}^{+3}$  compound is being oxidized to a  $\text{P}^{+5}$  compound, namely trimethyl phosphate,  $\text{O}=\text{P}(\text{OCH}_3)_3$ . This conversion is more predominant after one day. The band in the 1 day spectrum at 1384  $\text{cm}^{-1}$  is due to  $\text{KNO}_3$  from the KBr windows used to support the liquid film. Thus the resultant spectrum for trimethyl phosphite exposed to the atmosphere (over a period of 1 day) is not one of hydrolysis but one of oxidation to trimethyl phosphate. The sample also appears to be evaporating, so any longer exposure times are not practical.



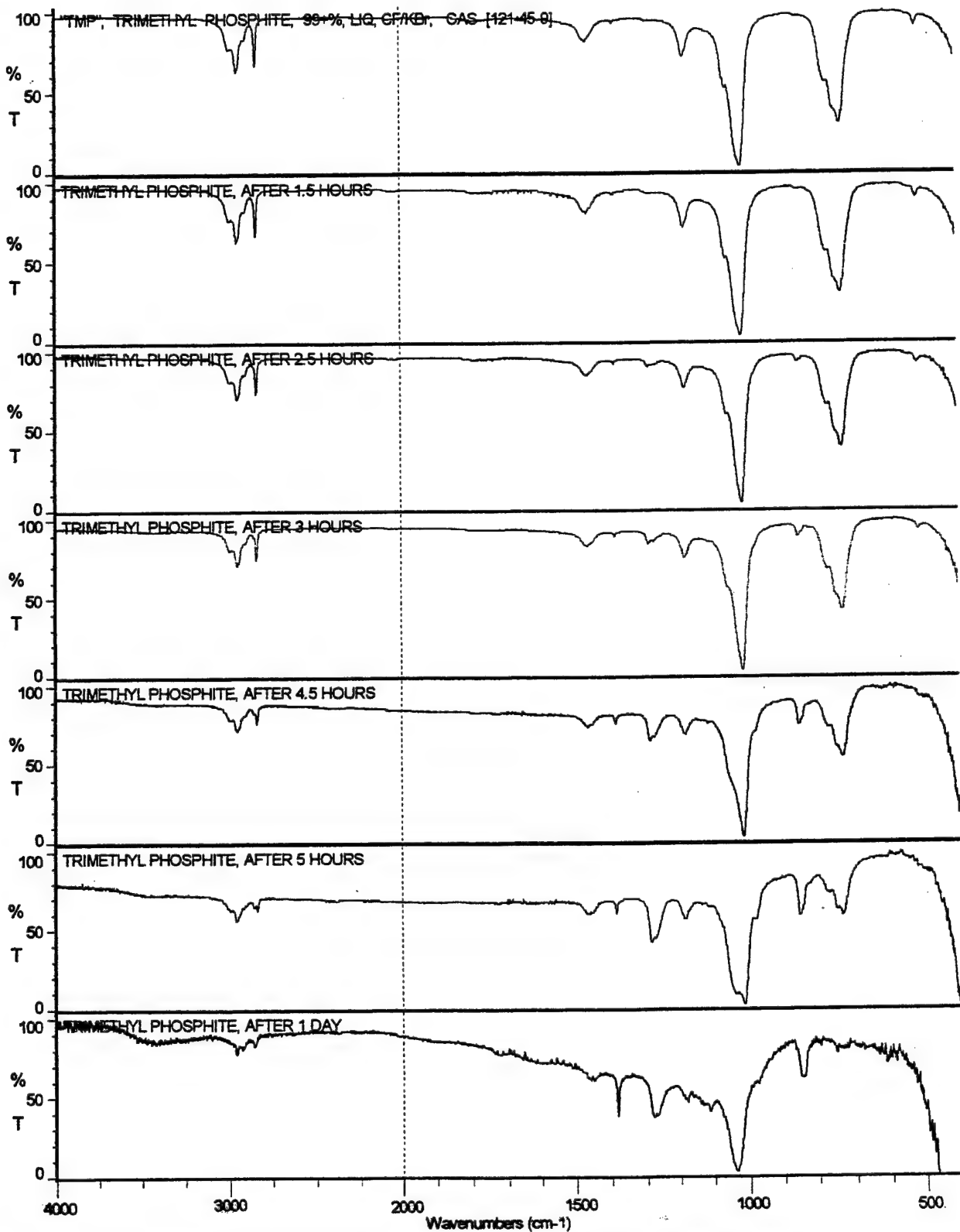
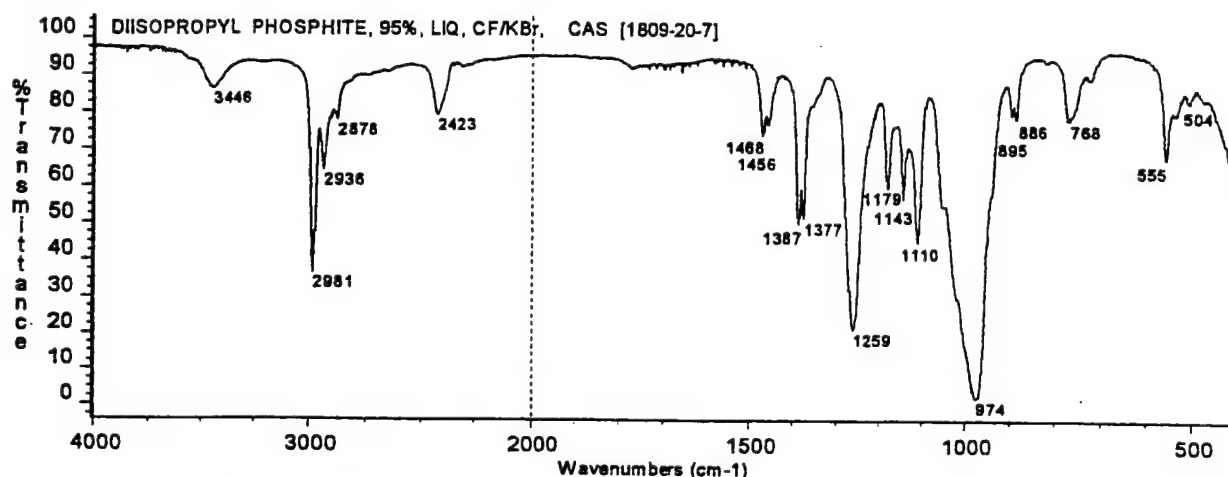


Figure 37 EFFECT OF THE ENVIRONMENT ON TRIMETHYL PHOSPHITE, LIQUID, CF/KBr

### 3.2.7 Diisopropyl Phosphite

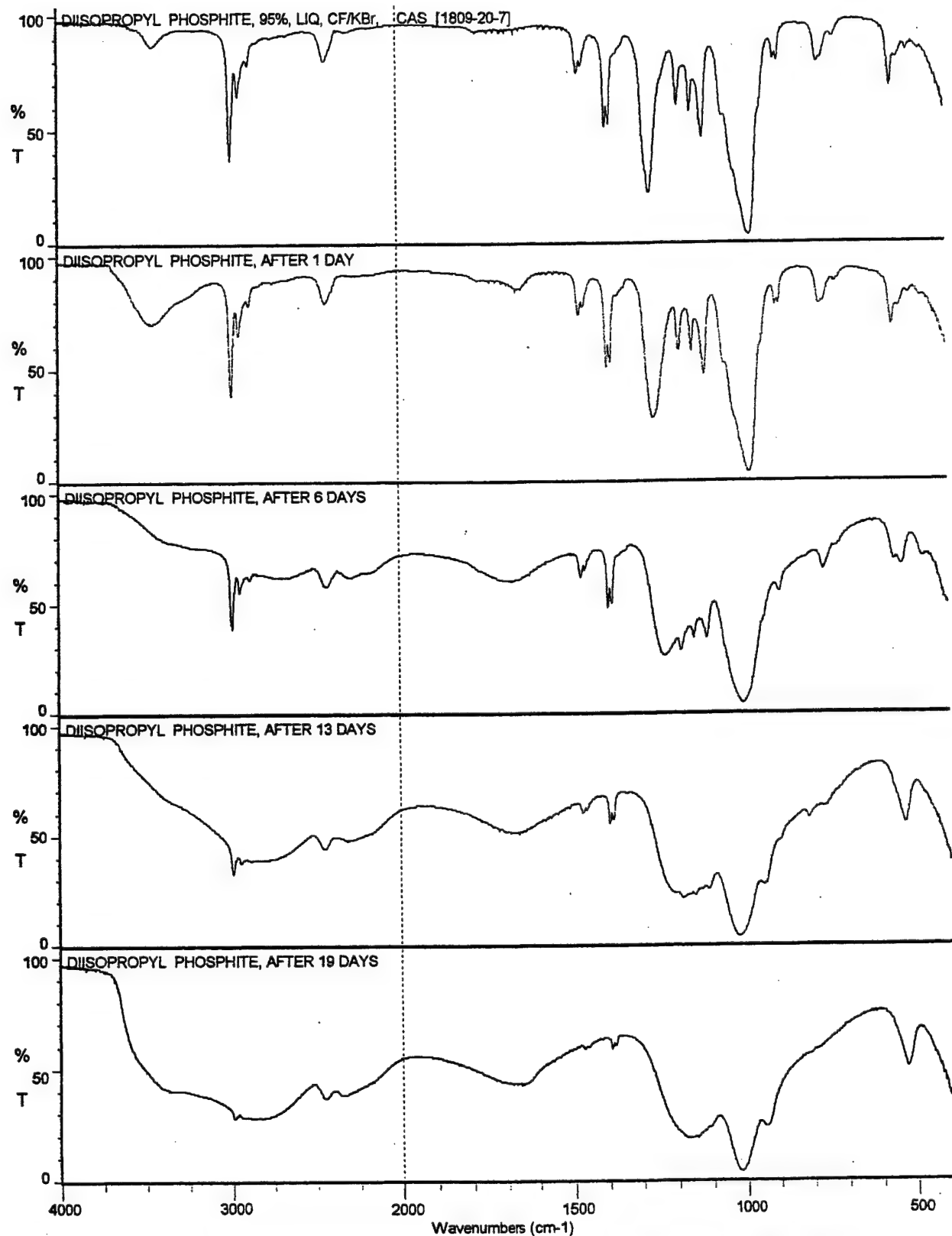


The infrared spectrum of diisopropyl phosphite is given in *Figure 38*. The band assignments are as follows: 3446  $\text{cm}^{-1}$  vw ( $\text{H}_2\text{O}$ ), 2981m, 2936 w and 2878  $\text{cm}^{-1}$  vw ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$  and  $\nu$  CH), 2423  $\text{cm}^{-1}$  w ( $\nu$  P-H), 1468  $\text{cm}^{-1}$  w and 1456  $\text{cm}^{-1}$  sh ( $\delta_{\text{as}}$   $\text{CH}_3$ ), 1387 and 1377  $\text{cm}^{-1}$  m (doublet,  $\delta_{\text{sy}}$   $\text{CH}_3$ ), ca 1354  $\text{cm}^{-1}$  sh ( $\delta$  C-H), 1259  $\text{cm}^{-1}$  ms ( $\nu$  P=O), 1179 w, 1143 w and 1110  $\text{cm}^{-1}$  m (a triplet characteristic of P-O-isopropyl), 974  $\text{cm}^{-1}$  s ( $\nu$  P-O-C and P-H deformation ?), 768  $\text{cm}^{-1}$  w (POC), 555  $\text{cm}^{-1}$  w ( $\delta$  P=O).

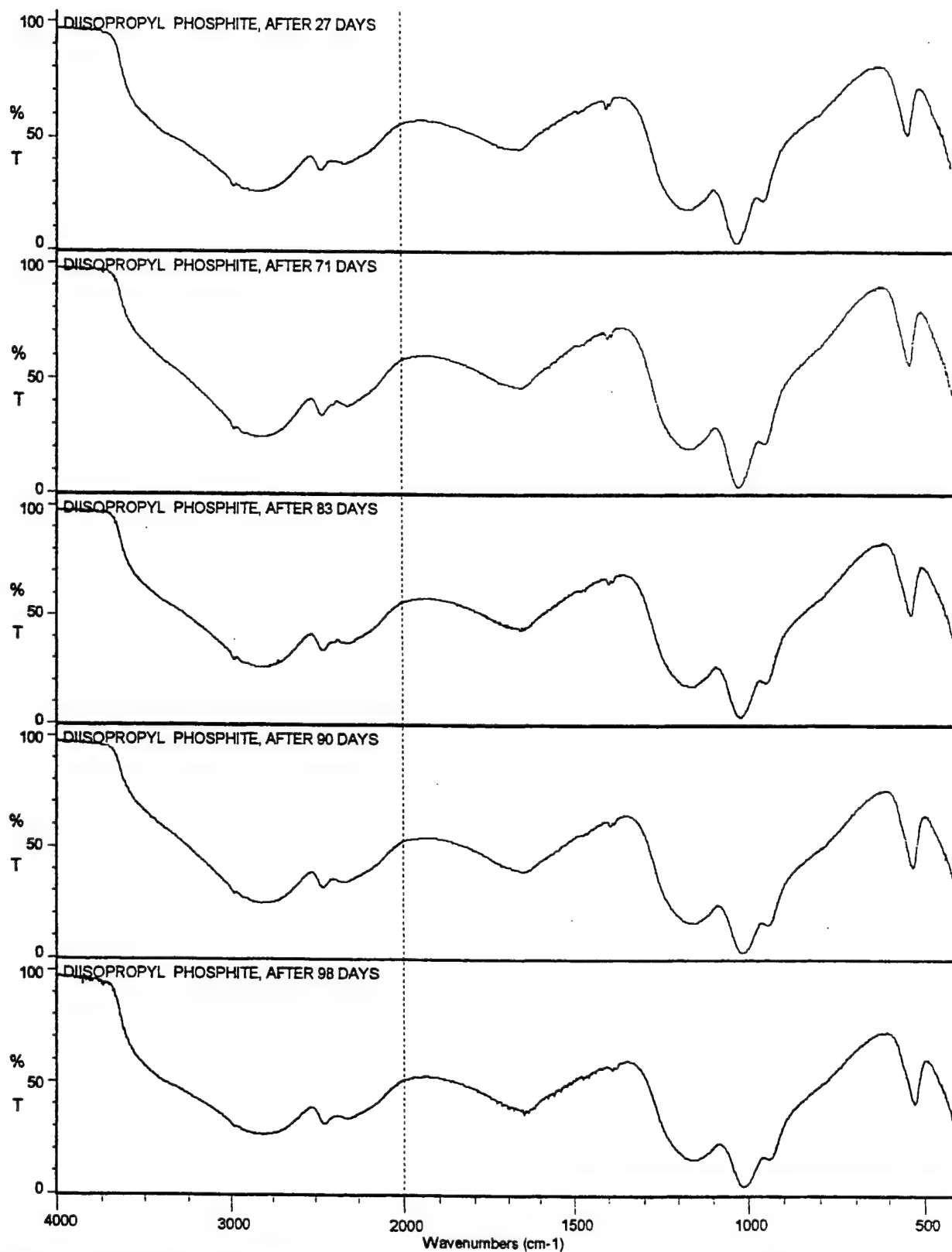


**Figure 38** DIISOPROPYL PHOSPHITE, 95%, LIQUID, CF/KBr

The effect of atmospheric moisture on diisopropyl phosphite is represented by the infrared spectra reproduced in *Figure 39*. After the first day the compound has picked up some water as evidenced by the bands at 3452 and 1653  $\text{cm}^{-1}$ . The  $\nu$  P=O has also decreased in value from 1259 to 1252  $\text{cm}^{-1}$  due to the water. After 6 days the spectrum resembles that of a P-acid with bands at ca 2700, 2280, 1675, 1225, and 1000  $\text{cm}^{-1}$  being due entirely or in part to the POOH moiety. The  $\nu$  P-H is still visible at 2423  $\text{cm}^{-1}$ . At the 13 day mark the bands due to isopropyl moiety have become much weaker. One of the O-isopropyl groups has been hydrolyzed off to leave the resultant compound,  $\text{H}-\text{P}=\text{O}(\text{OH})(\text{O-isopropyl})$ . As time progresses the bands assignable to the isopropyl moiety have almost completely disappeared from the infrared spectra. The resultant compound after the 98<sup>th</sup> day appears to be almost entirely phosphorous acid,  $\text{H}_3\text{PO}_3$ , that is,  $\text{H}-\text{P}=\text{O}(\text{OH})_2$ . The hydrolysis may be represented as follows:  $\text{HP}=\text{O}(\text{O-iPr})_2 -\text{HOH}-> \text{HP}=\text{O}(\text{OH})(\text{O-iPr}) -\text{HOH}-> \text{HP}=\text{O}(\text{OH})_2$ .



**Figure 39 EFFECT OF ATMOSPHERIC MOISTURE ON DIISOPROPYL PHOSPHITE, LIQUID, CF/KBr**



**Figure 39** EFFECT OF ATMOSPHERIC MOISTURE ON DIISOPROPYL PHOSPHITE, LIQUID, CF/KBr  
(CONTINUED)

## 3.2.8 Triisopropyl Phosphite



The infrared spectrum of triisopropyl phosphite is given in *Figure 40*. The band assignments are as follows: 2974  $\text{cm}^{-1}$  ms, 2932  $\text{cm}^{-1}$  m, and 2876  $\text{cm}^{-1}$  w ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$ ), 1466 and 1453  $\text{cm}^{-1}$  w ( $\delta_{\text{as}}$   $\text{CH}_3$ ), 1383 and 1371  $\text{cm}^{-1}$  m doublet ( $\delta_{\text{sy}}$   $\text{CH}_3$ ), 1351  $\text{cm}^{-1}$  w ( $\delta$  C-H), 1280 and 1263  $\text{cm}^{-1}$  vw ( $\nu$  P=O of triisopropyl phosphate ?), 1176  $\text{cm}^{-1}$  m, 1138  $\text{cm}^{-1}$  m and 1109  $\text{cm}^{-1}$  ms (characteristic of P-O-isopropyl), 1000  $\text{cm}^{-1}$  m and 957  $\text{cm}^{-1}$  ms ( $\nu$  P-O-C), 858  $\text{cm}^{-1}$  ms ( $\text{CH}_3$  rock of isopropyl group), 771 and 741  $\text{cm}^{-1}$  m (POC), 541  $\text{cm}^{-1}$  w (P=O deformation ?).

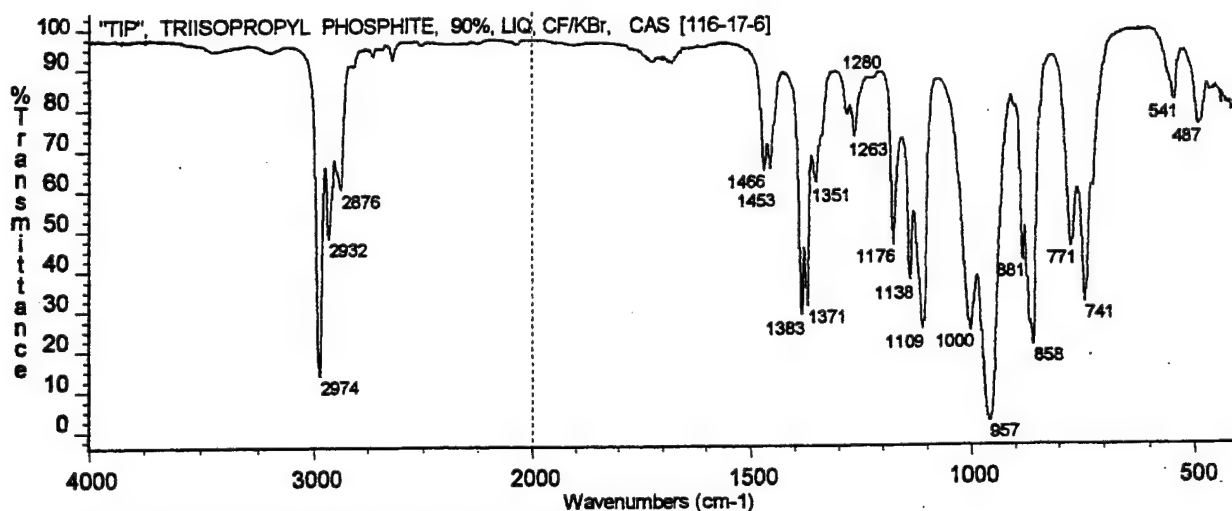


Figure 40 TRIISOPROPYL PHOSPHITE, 90%, LIQUID, CF/KBr

The effect of atmospheric moisture on triisopropyl phosphite is presented in *Figure 41*. After 19 hours of exposure to atmospheric moisture the infrared spectrum show a very weak band at 2425  $\text{cm}^{-1}$  due to P-H stretching. The bands at 1278 and 1262  $\text{cm}^{-1}$  are increasing in intensity. Apparently two effects are occurring. On the one hand, hydrolysis is occurring to produce possibly  $\text{H}-\text{P}=\text{O}(\text{O}-i\text{Pr})_2$ , while concurrently oxidation is causing the formation of  $\text{O}=\text{P}(\text{O}-i\text{Pr})_3$ . However, after 7 days have elapsed, the P-H stretching band at 2425  $\text{cm}^{-1}$  seems to have disappeared from the spectrum. The bands at 1275 and 1261  $\text{cm}^{-1}$  are still present and are assigned to the P=O stretching of trisopropyl phosphate. By the eighth day, the P=O stretching band has a low frequency component near 1230  $\text{cm}^{-1}$ , which may be the beginning of P-acid formation. There appears to be some very weak diffuse absorption near 3000 and

2300  $\text{cm}^{-1}$  which could be indicative of P-OH formation.

Thus, some of the compound appears to undergo hydrolysis as follows:  $\text{P}(\text{O-iPr})_3 \xrightarrow{-\text{HOH}}$   $\text{H-P}=\text{O}(\text{O-iPr})_2$ . The rest of the compound oxidizes and then may hydrolyze as follows:  $\text{P}(\text{O-iPr})_3 \xrightarrow{-[\text{O}]}$   $\text{O}=\text{P}(\text{O-iPr})_3 \xrightarrow{-\text{HOH}}$   $\text{HO-P}=\text{O}(\text{O-iPr})_2$ . The sample appears to be evaporating with the passage of time, so that the diisopropyl phosphite formed disappears leaving the triisopropyl phosphate formed, which then begins to hydrolyze to form the P-acid.

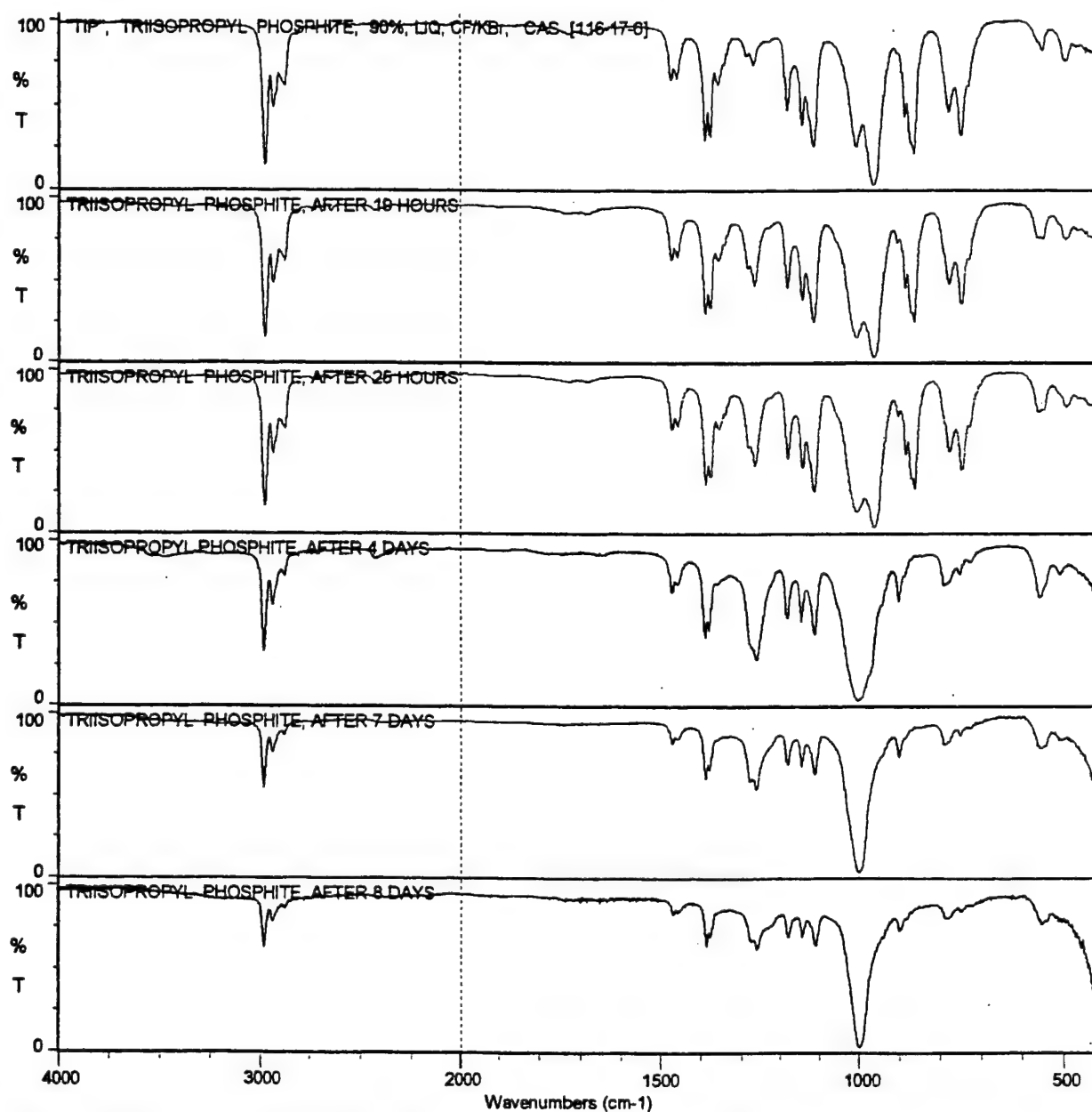


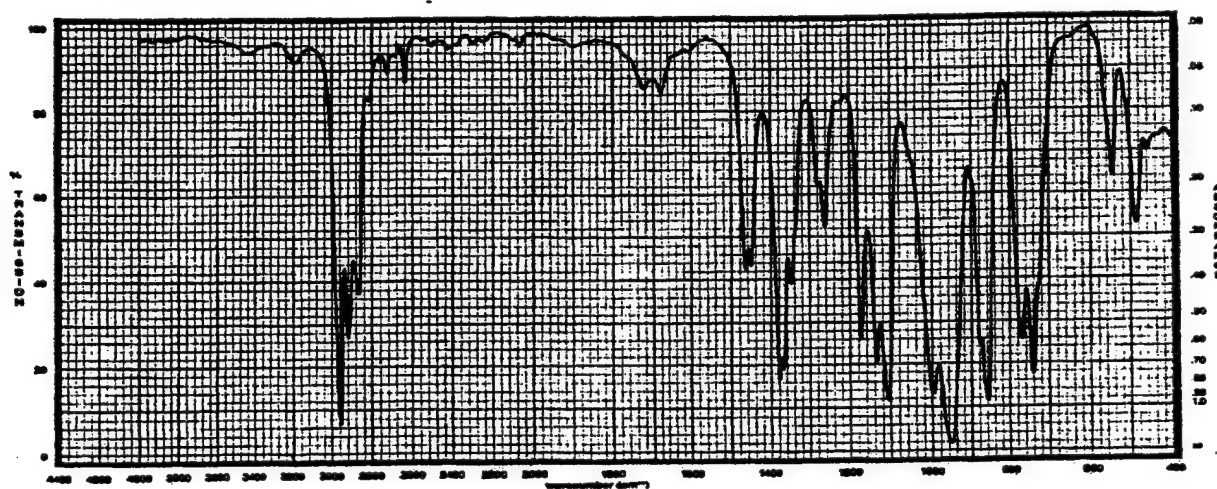
Figure 41 EFFECT OF ATMOSPHERIC MOISTURE ON TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr

Some time later, another sample of triisopropyl phosphite was determined as a liquid film between KBr windows (discs). The effect of the environment on this sample is given in *Figures 42A through 42F*. The infrared spectrum given in *Figure 42A* is similar to that given in *Figure 40*. Both



**Figure 42A TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr**

figures show the presence of P=O stretching near  $1275$  and  $1260\text{ cm}^{-1}$  that is attributed to triisopropyl phosphate,  $\text{O}=\text{P}(\text{O}-i\text{Pr})_3$ . This is still the picture after 5 hours of exposure to the environment. However, after 22 hours, the spectrum (*Figure 42 C*) shows a new band at  $2426\text{ cm}^{-1}$  due to the  $\nu\text{ P-H}$ , and a band



**Figure 42 B TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER 5 HOURS OF ENVIRONMENTAL EXPOSURE**

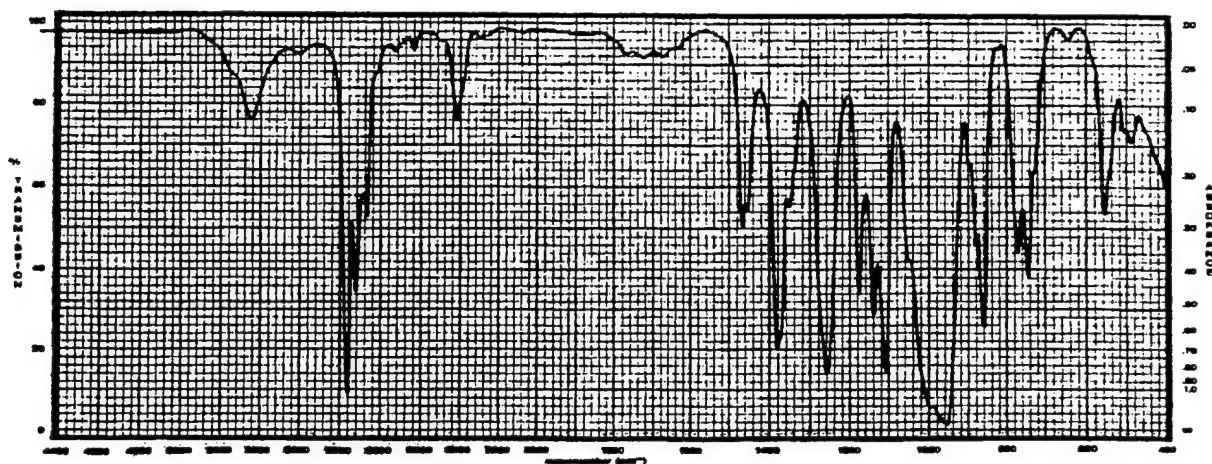


Figure 42 C TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER 22 HOURS OF ENVIRONMENTAL EXPOSURE

at  $1260\text{ cm}^{-1}$  due to a  $\text{P}=\text{O}$  stretching vibration., as well as bands at 1179, 1143 and  $1110\text{ cm}^{-1}$  (characteristic of  $\text{P}-\text{O}-i\text{Pr}$ ). These bands are believed to be from diisopropyl phosphite,  $\text{H}-\text{P}=\text{O}(\text{O}-i\text{Pr})_2$ , formed as a result of hydrolysis. The infrared spectra for the period 70 hours (Figure 42D) to 4 days (Figure 42E) still show the presence of diisopropyl phosphite (see Figure 38 for comparison to an authentic diisopropyl phosphite). At the 7 day mark the infrared spectrum (Figure 42F) is totally different from the spectra that preceded it. An examination of the sample between the KBr discs showed only a small spot of sample remaining. Apparently the sample present at the 4 day mark (diisopropyl phosphite) evaporated leaving behind a sample believed to be triisopropyl phosphate. This new compound would result from the oxidation of the original triisopropyl phosphite.

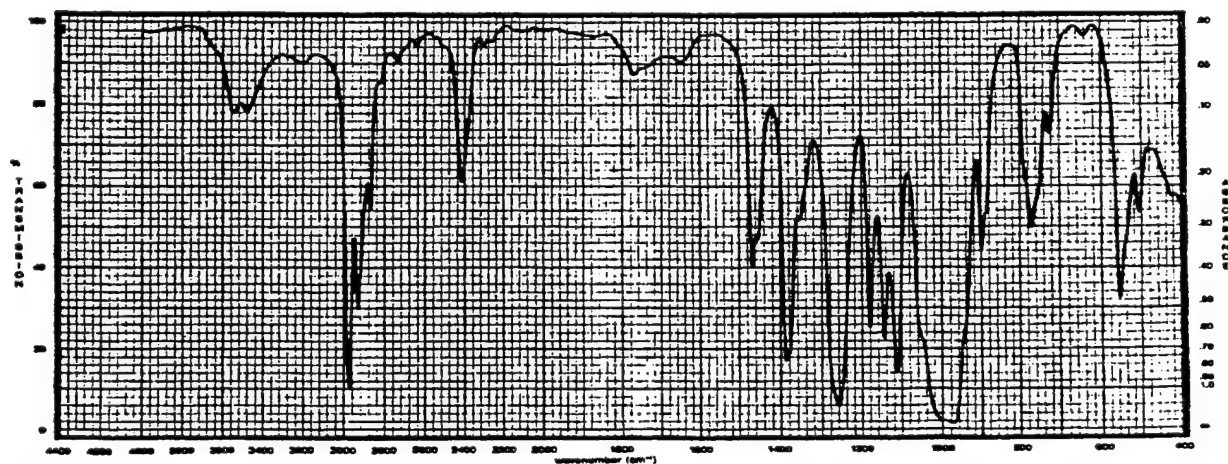


Figure 42D TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER 70 HOURS OF ENVIRONMENTAL EXPOSURE



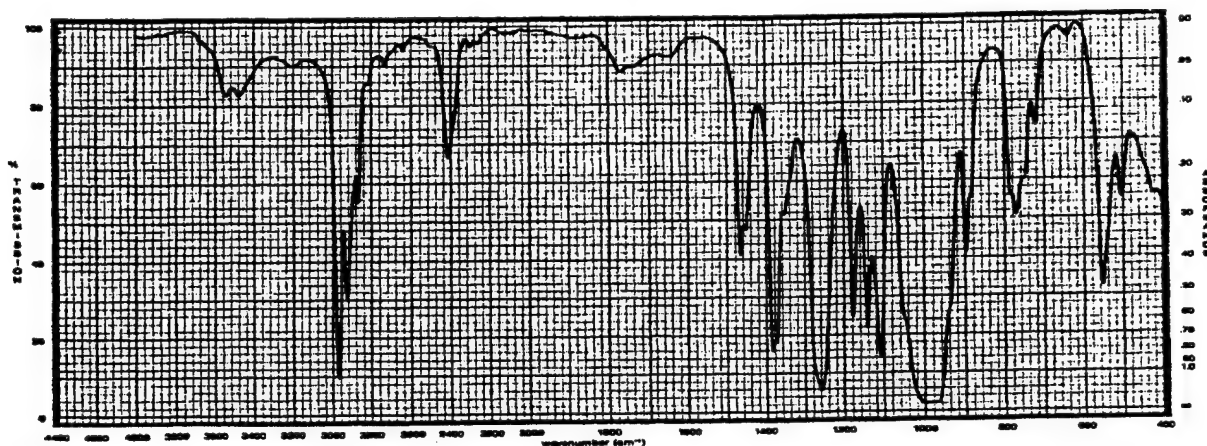


Figure 42E TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER 4 DAYS OF ENVIRONMENTAL EXPOSURE

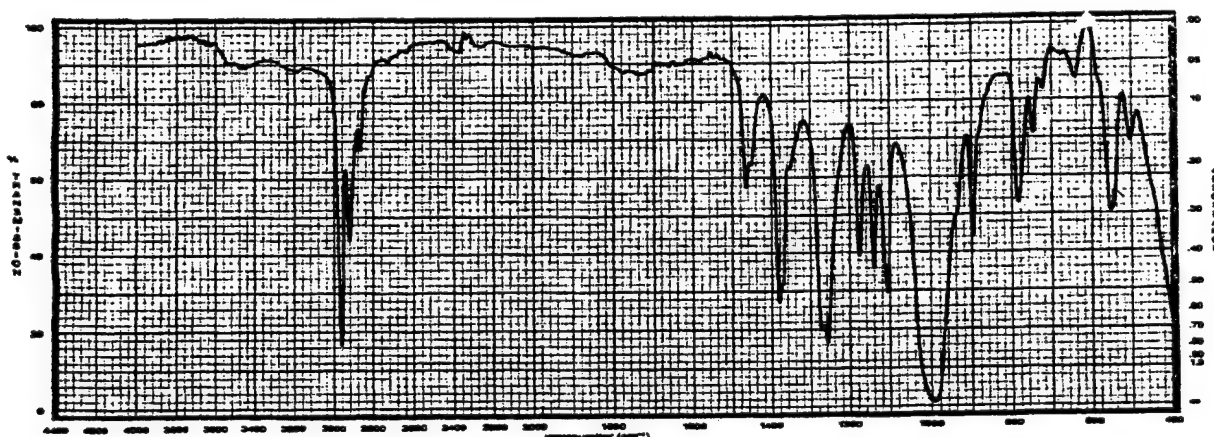
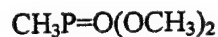


Figure 42F TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER 7 DAYS OF ENVIRONMENTAL EXPOSURE

### 3.2.9 Dimethyl Methylphosphonate (DMMP)



The infrared spectrum of dimethyl methylphosphonate (DMMP) is given in *Figure 43*. The band assignments are as follows: 2994  $\text{cm}^{-1}$  vw and 2926  $\text{cm}^{-1}$  vw ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$ ), 2956  $\text{cm}^{-1}$  w and 2852  $\text{cm}^{-1}$  w ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{OCH}_3$ ), 1465  $\text{cm}^{-1}$  w ( $\delta$   $\text{OCH}_3$ ), 1420  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$   $\text{P-CH}_3$ ), 1313  $\text{cm}^{-1}$  m ( $\delta_{\text{sy}}$   $\text{P-CH}_3$ ), 1245  $\text{cm}^{-1}$  ms ( $\nu$   $\text{P=O}$ ), 1185  $\text{cm}^{-1}$  w ( $\text{CH}_3$  rock, characteristic of  $\text{POCH}_3$ ), 1058  $\text{cm}^{-1}$  sh and 1032  $\text{cm}^{-1}$  s ( $\nu$   $\text{P-O-C}$ ), 914  $\text{cm}^{-1}$  m ( $\text{P-CH}_3$  rock), 819  $\text{cm}^{-1}$  m and 788  $\text{cm}^{-1}$  m ( $\text{POC}$ ), 713  $\text{cm}^{-1}$  w ( $\nu$   $\text{P-C}$ ), 501  $\text{cm}^{-1}$  w ( $\text{P=O}$  deformation ?).

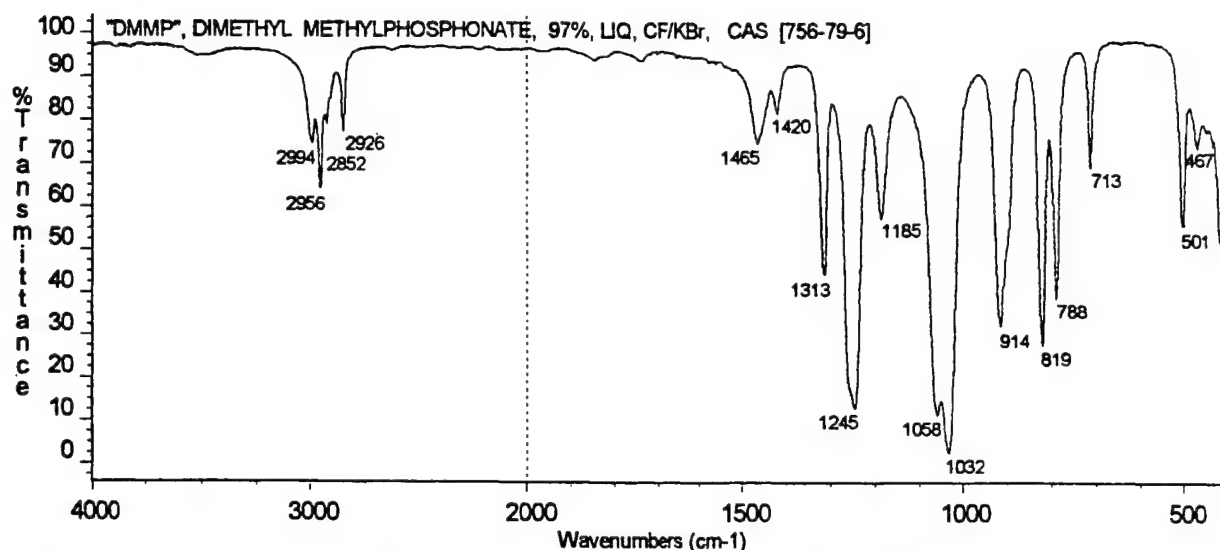
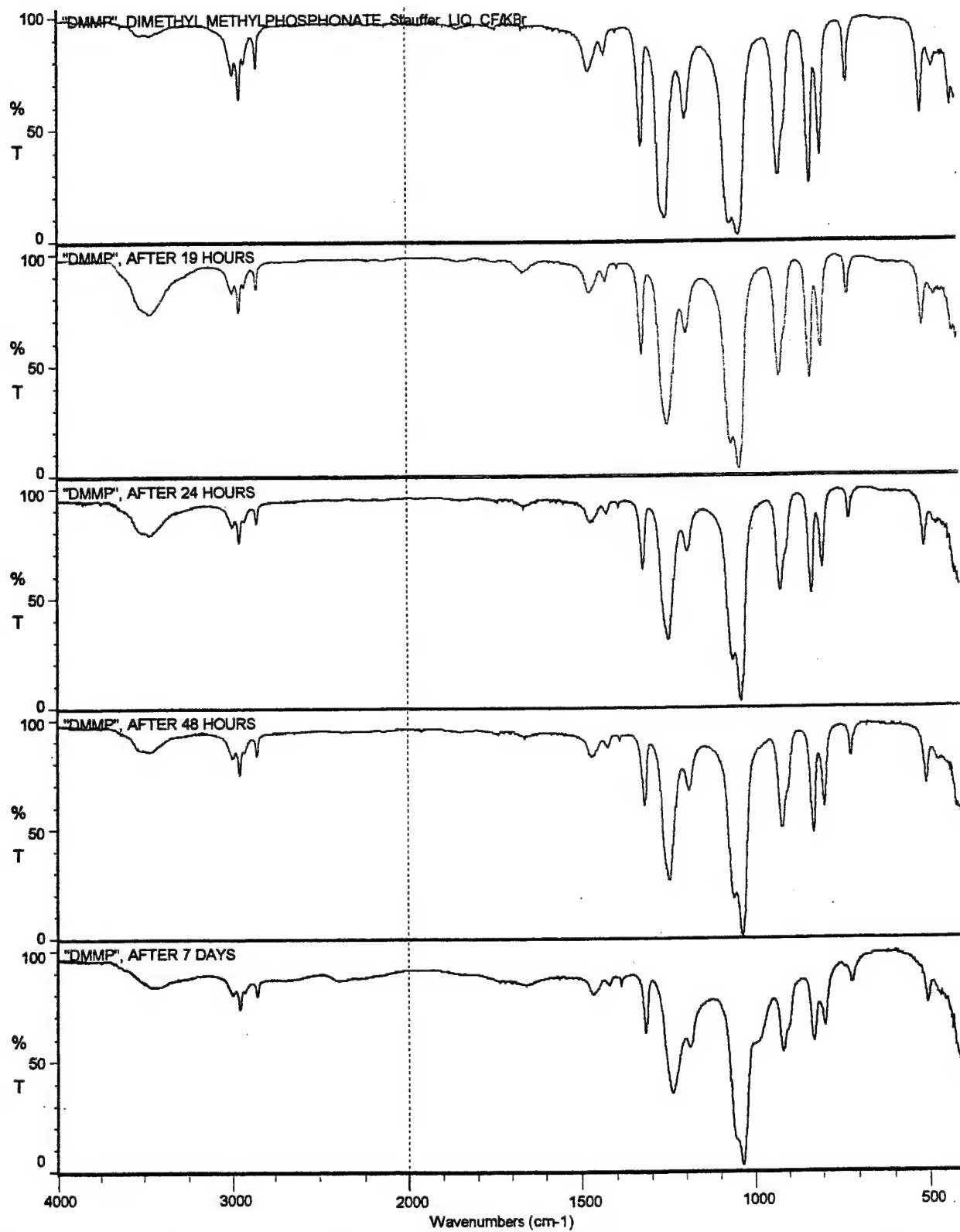


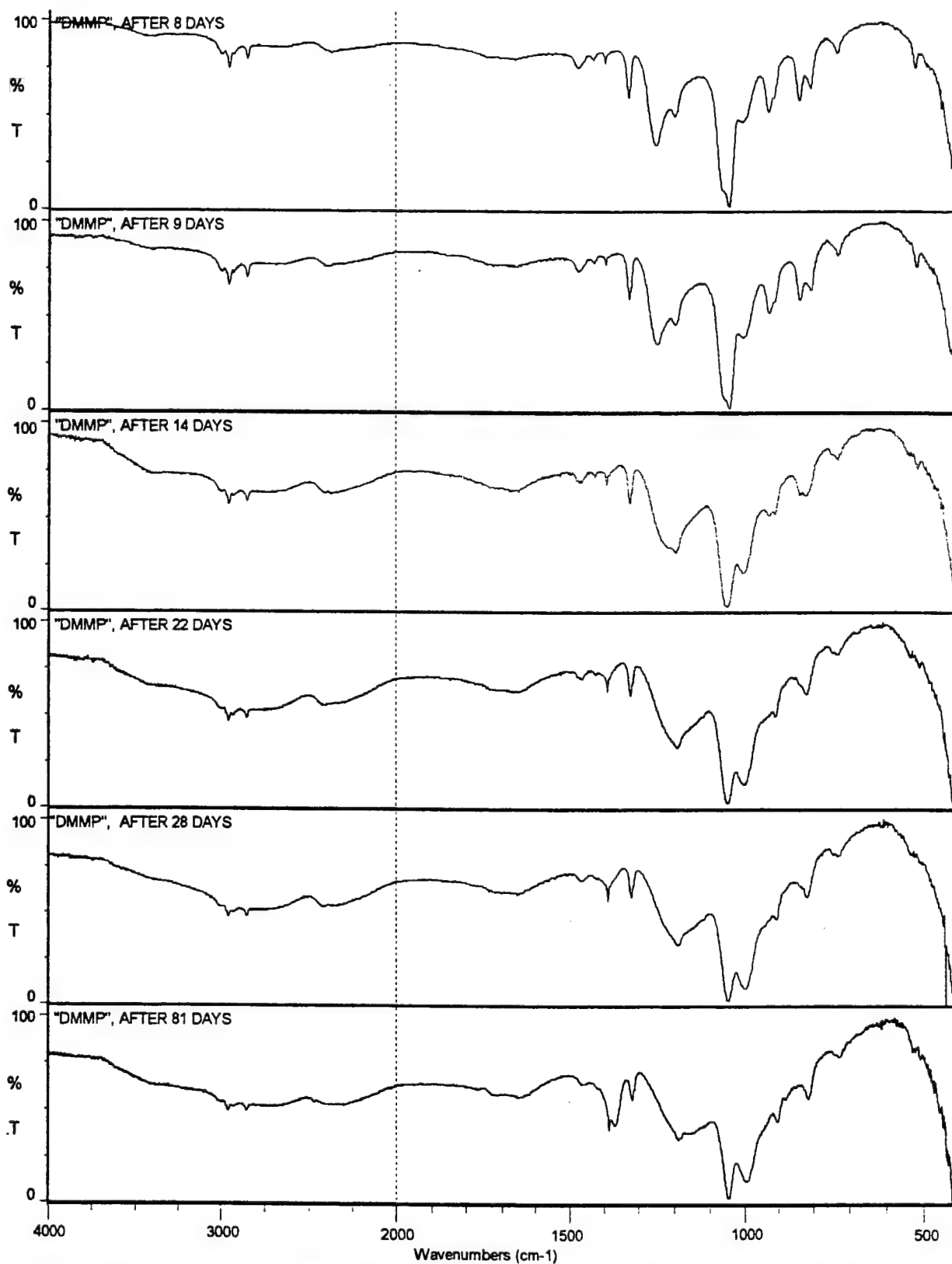
Figure 43 DIMETHYL METHYLPHOSPHONATE (DMMP), 97%, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin liquid film of dimethyl methylphosphonate (DMMP) between KBr windows is given in *Figure 44*. As the 7<sup>th</sup> day period is approached, the sample has picked up water. This is evidenced by the bands near 3470 and 1650  $\text{cm}^{-1}$  and the decrease in the P=O stretching vibration from 1246 to 1238  $\text{cm}^{-1}$ . Very weak broad bands are also visible near 2800 and 2370  $\text{cm}^{-1}$  that indicate the presence of a P-acid (i.e., POOH). These acid bands become increasingly stronger as time passes. At the 14 day mark, POH bands are quite evident at ca 2800, 2370, 1650 and 995  $\text{cm}^{-1}$ . The P=O stretching band has decreased to ca 1200  $\text{cm}^{-1}$ ; the POCH<sub>3</sub> moiety is still present as indicated by the bands at 1187 and 1037  $\text{cm}^{-1}$ . The resident species may now be methyl hydrogen methylphosphonate (or methyl methylphosphonic acid),  $\text{CH}_3\text{P}=\text{O}(\text{OH})(\text{OCH}_3)$ .<sup>b</sup> During the 22<sup>d</sup> through 81<sup>st</sup> day time period, the compound may be hydrolyzing further as indicated by the slight broadening of the band below 1186  $\text{cm}^{-1}$ . A new compound such as methylphosphonic acid,  $\text{CH}_3\text{P}=\text{O}(\text{OH})_2$ , may be forming. The hydrolysis of dimethyl methylphosphonate may be represented as follows:  $\text{CH}_3\text{P}=\text{O}(\text{OCH}_3)_2 -\text{HOH}-> \text{CH}_3\text{P}=\text{O}(\text{OH})(\text{OCH}_3) -\text{HOH}-> \text{CH}_3\text{P}=\text{O}(\text{OH})_2$ .

<sup>b</sup> An infrared spectrum for this compound is reproduced in "Chemical and Instrumental Verification of Organophosphorus Warfare Agents", p 76, Figure 8.27. Prepared for The Ministry for Foreign Affairs of Finland by the Advisory Board for Disarmament, Helsinki, 1977.

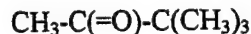


**Figure 44 EFFECT OF ATMOSPHERIC MOISTURE ON DIMETHYL METHYLPHOSPHONATE (DMMP), LIQUID, CF/KBr**



**Figure 44 EFFECT OF ATMOSPHERIC MOISTURE ON DIMETHYL METHYLPHOSPHONATE (DMMP), LIQUID, CF/KBr (CONTINUED)**

### 3.2.10 3,3-Dimethylbutanone-2 (Pinacolone)



The infrared spectrum of 3,3-dimethylbutanone-2 or *t*-butyl methyl ketone (**pinacolone**), is given in **Figure 45**. The band assignments are as follows: 3398  $\text{cm}^{-1}$  vw (overtone of  $\nu \text{ P=O}$ ,  $2 \times 1709 = 3418 \text{ cm}^{-1}$ ), 2971  $\text{cm}^{-1}$  ms, 2909  $\text{cm}^{-1}$  w and 2873  $\text{cm}^{-1}$  m ( $\nu \text{ CH}_3$ ), 1709  $\text{cm}^{-1}$  s ( $\nu \text{ C=O}$ ), 1478  $\text{cm}^{-1}$  m and 1466  $\text{cm}^{-1}$  sh ( $\delta_{\text{as}} \text{ CH}_3$ ), 1429  $\text{cm}^{-1}$  w ( $\delta_{\text{as}} \text{ CH}_3\text{-C=O}$ ), 1394  $\text{cm}^{-1}$  w ( $\delta_{\text{sy}} \text{ CH}_3 \text{ } t\text{-butyl}$ ), 1366 and 1355  $\text{cm}^{-1}$  ms ( $\delta_{\text{sy}} \text{ CH}_3 \text{ of } t\text{-butyl and CH}_3\text{-C=O}$ ), 1274  $\text{cm}^{-1}$  m and 1223  $\text{cm}^{-1}$  vw (*t*-butyl ?), 1137  $\text{cm}^{-1}$  ms (ketone  $\nu \text{ C-C-C}$ ), 954  $\text{cm}^{-1}$  m ( $\text{CH}_3 \text{ rock}$ ), 554  $\text{cm}^{-1}$  m ( $\text{C=O deformation ?}$ ).

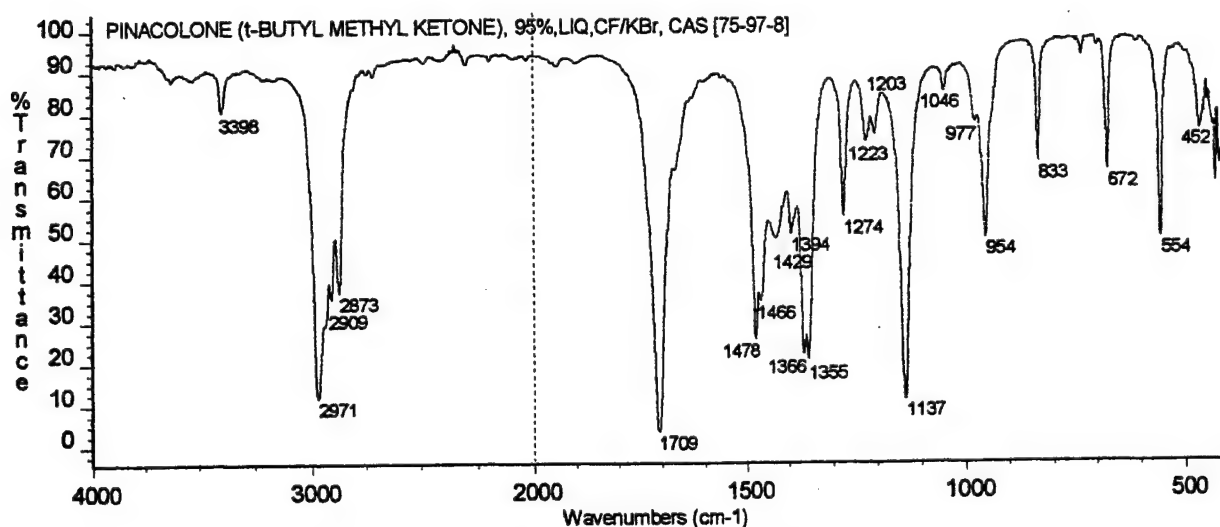


Figure 45 PINACOLONE (3,3-DIMETHYLBUTANONE-2), 95%, LIQUID, CF/KBr

### 3.3 Decomposition Products of G-Agents

Isopropyl methylphosphonic acid (isopropyl hydrogen methylphosphonate), **IMPA**, **GB Acid**,

CAS [5514-35-2]

Methyl phosphonic acid (**MPA**), CAS [993-13-5]

Methyphosphonic anhydride

Methylphosphonic difluoride (**DF**, **Difluor**), CAS [676-99-3]

Methylphosphonofluoridic acid (**Fluoro Acid**), CAS [1511-67-7]

Diisopropyl methylphosphonate (**DIMP**), CAS [1445-75-6]

2-Propanol (isopropyl alcohol, isopropanol), CAS [67-63-0]

Cyclohexyl methylphosphonic acid (cyclohexyl hydrogen methylphosphonate), **GF Acid**,  
CAS [1932-60-1]

Pinacolyl methylphosphonic acid (1,2,2-trimethylpropyl hydrogen methylphosphonate), **GD Acid**, CAS [616-52-4]

Dipinacolyl methylphosphonate [bis(1,2,2-trimethylpropyl) methylphosphonate], CAS  
[7040-58-6]

Pinacolyl alcohol (3,3-dimethyl-2-butanol or 1,2,2-trimethyl-1-propanol), CAS [464-07-3]

2-Methylcyclohexyl methylphosphonic acid (2-methylcyclohexyl hydrogen methylphosphonate), **EA 1356 Acid**

### 3.3.1 Isopropyl Methylphosphonic Acid (Isopropyl Hydrogen Methylphosphonate), IMPA



The infrared spectrum of isopropyl methylphosphonic acid (**IMPA, GB Acid**) or isopropyl hydrogen methylphosphonate is given in *Figure 46*. The band assignments are as follows: 2981  $\text{cm}^{-1}$  m, 2934  $\text{cm}^{-1}$  w and 2878  $\text{cm}^{-1}$  vw ( $\nu$   $\text{CH}_3$ ), 2639  $\text{cm}^{-1}$ , 2292  $\text{cm}^{-1}$  and 1685  $\text{cm}^{-1}$  (all weak and broad, characteristic of the acid POH), 1469  $\text{cm}^{-1}$  vw and 1457  $\text{cm}^{-1}$  sh ( $\delta_{\text{as}}$   $\text{CH}_3$ ), 1420  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ), 1376 and 1387  $\text{cm}^{-1}$  weak doublet (characteristic of isopropyl group,  $\delta_{\text{sy}}$   $\text{CH}_3$ ), ca 1350  $\text{cm}^{-1}$  sh ( $\delta$  -CH), 1313  $\text{cm}^{-1}$  m ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ), 1203  $\text{cm}^{-1}$  ms ( $\nu$  P=O), 1179  $\text{cm}^{-1}$ , 1143  $\text{cm}^{-1}$  and 1108  $\text{cm}^{-1}$  (weak triplet of bands characteristic of P-O-isopropyl), 1004  $\text{cm}^{-1}$  s ( $\nu$  P-O-C and  $\nu$  P-OH), 906  $\text{cm}^{-1}$  w (P- $\text{CH}_3$  rock), 877  $\text{cm}^{-1}$  vw (isopropyl  $\text{CH}_3$  rock), 783  $\text{cm}^{-1}$  w (POC), 730  $\text{cm}^{-1}$  vw ( $\nu$  P-C), 510  $\text{cm}^{-1}$  w (P=O deformation ?).

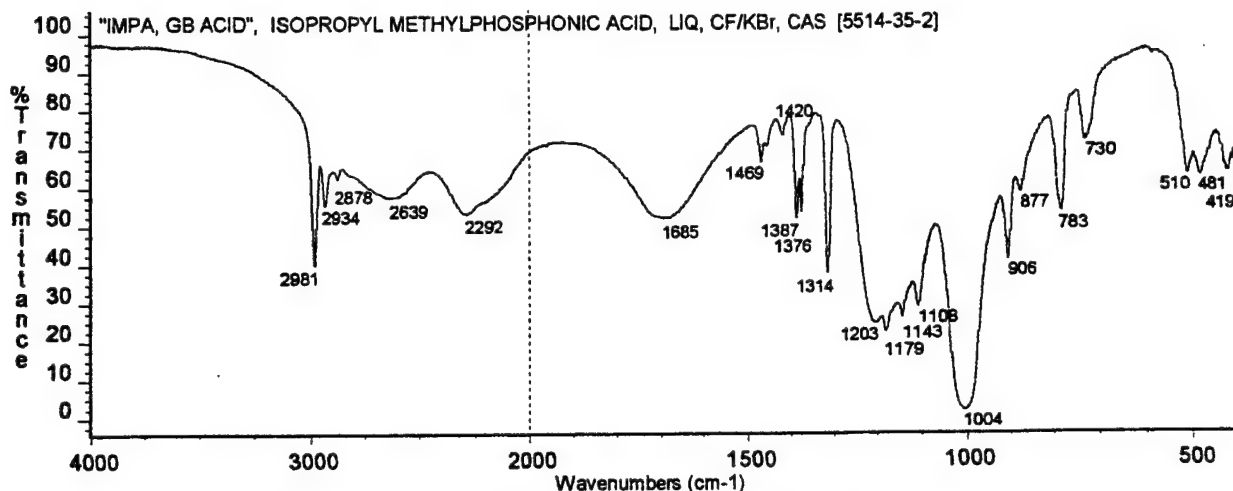


Figure 46 ISOPROPYL METHYLPHOSPHONIC ACID (IMPA), LIQUID, CF/KBr

### 3.3.2 Methylphosphonic Acid (MPA) $\text{CH}_3\text{P}=\text{O}(\text{OH})_2$

The infrared spectrum of methylphosphonic acid (MPA) is given in *Figure 47*. The band assignments are as follows: 3013 and 2934  $\text{cm}^{-1}$  vvw ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$ ), 2744  $\text{cm}^{-1}$  m broad, 2337  $\text{cm}^{-1}$  m and ca 1630  $\text{cm}^{-1}$  vw (characteristic of POH), 1534  $\text{cm}^{-1}$  vvw ( $2 \times 767 = 1534 \text{ cm}^{-1}$ ), 1423 and 1415  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ), 1323  $\text{cm}^{-1}$  m ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ), 1260  $\text{cm}^{-1}$  m (P-OH in-plane bend ?), 1155  $\text{cm}^{-1}$  m ( $\nu$  P=O ?), 1011 and 954  $\text{cm}^{-1}$  s ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$  P-OH), 891  $\text{cm}^{-1}$  vw (P- $\text{CH}_3$  rock ?), 767  $\text{cm}^{-1}$  ms ( $\nu$  P-C), 495 m and 458  $\text{cm}^{-1}$  (P=O deformation ?).

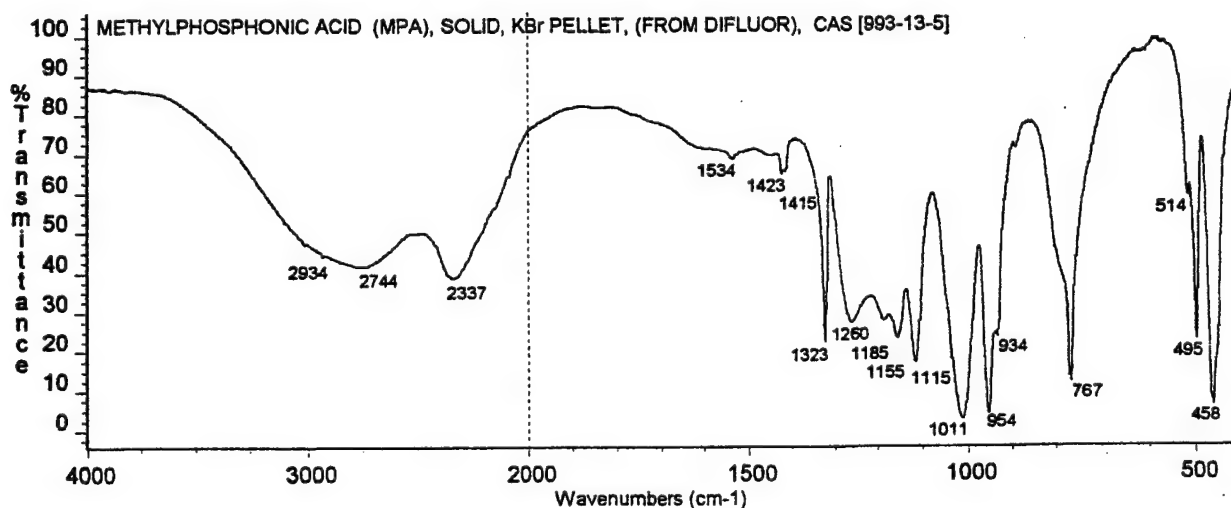


Figure 47 METHYLPHOSPHONIC ACID (MPA), SOLID, KBr PELLET

If the KBr pellet containing methylphosphonic acid is reground and repressed a number of times, one begins to see changes occurring in the infrared spectrum with each remaking of the pellet. This effect is illustrated in *Figure 48*. The resultant infrared spectra, after the sixth and seventh regrindings and repressings of the KBr pellets, show that the compound is no longer methylphosphonic acid but more probably the salt of the acid. The infrared spectrum now shows a strong band at 1093-1083  $\text{cm}^{-1}$  ( $\nu_{\text{as}} \text{PO}_3^{-2}$ ) and a much weaker band near 950  $\text{cm}^{-1}$  ( $\nu_{\text{sy}} \text{PO}_3^{-2}$ ). Other bands at 2995  $\text{cm}^{-1}$  vvw, 2928  $\text{cm}^{-1}$  vvw, 1420  $\text{cm}^{-1}$  vvw, 1312  $\text{cm}^{-1}$  w, 874  $\text{cm}^{-1}$  vvw and 771  $\text{cm}^{-1}$  w are due to the P-CH<sub>3</sub> group. Therefore, with increased grinding of the sample/KBr matrix changes occur to produce a salt of methylphosphonic acid [ $\text{CH}_3\text{-P=O(OH)}_2 \rightarrow \text{CH}_3\text{-PO(O}^-\text{K}^+)_2$ ]. This example illustrates the care that must be exercised in the grinding of samples for use in the KBr pellet technique.



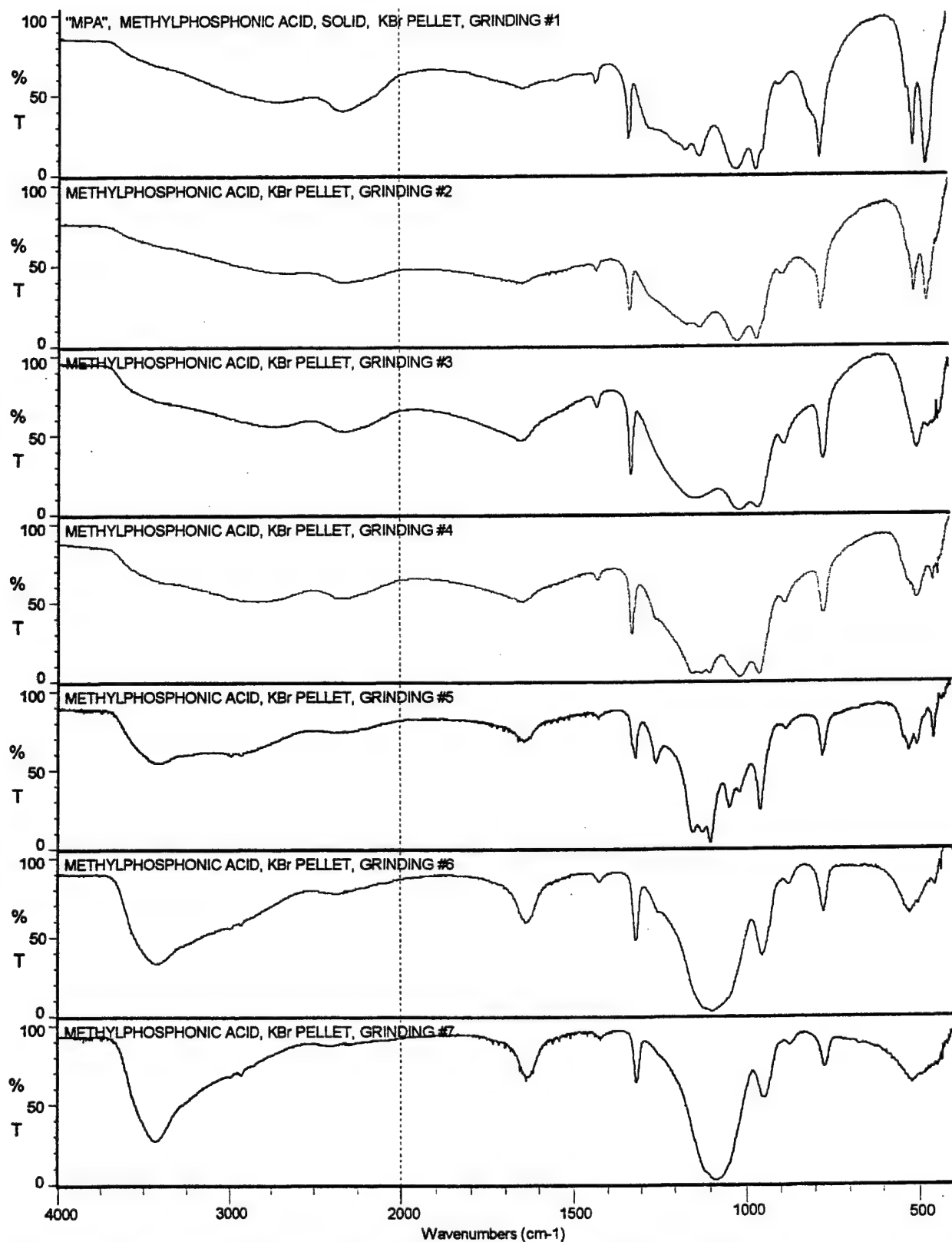
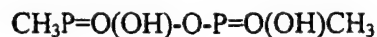


Figure 48 EFFECT OF GRINDING ON THE METHYLPHOSPHONIC ACID/KBr MATRIX

### 3.3.3 Methylphosphonic Anhydride



The infrared spectrum of methylphosphonic anhydride is reproduced in *Figure 49*. The band assignments are as follows: 3006  $\text{cm}^{-1}$  vw and 2929  $\text{cm}^{-1}$  vw ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$ ), 2633  $\text{cm}^{-1}$ , 2305  $\text{cm}^{-1}$  and 1679  $\text{cm}^{-1}$  all weak and broad (POH), 1424  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ), 1311  $\text{cm}^{-1}$  m ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ), 1213  $\text{cm}^{-1}$  ms ( $\nu$  P=O), 1009  $\text{cm}^{-1}$  ms ( $\nu$  P-OH), 951  $\text{cm}^{-1}$  ms ( $\nu$  P-O-P), 775 s ( $\nu$  P-C), 525 w, 504 m, 468 m, 445 ms  $\text{cm}^{-1}$  (P=O deformations?).

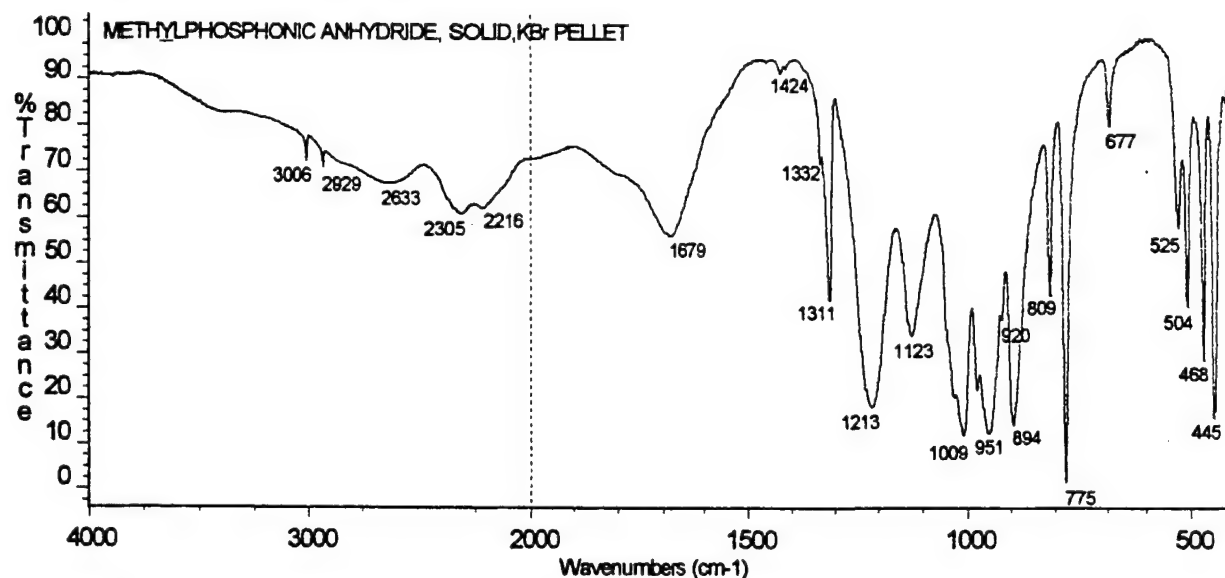


Figure 49 METHYLPHOSPHONIC ANHYDRIDE, SOLID, KBr PELLET

In *Figure 50*, the effect of grinding on the solid/KBr matrix is illustrated. The top most spectrum is from a freshly prepared pellet. The next spectrum is from another freshly prepared pellet. Note the differences in the band intensities between the two spectra. The third spectrum down shows the previous pellet reground and repressed. Note this spectrum appears to lie between the two previous spectra. The last spectrum in the group, shows the effect of moisture on the pellet after it had been sitting in the air for 6 days. This last pellet now seems to resemble the spectrum for methylphosphonic acid (*Figure 48*, grinding #3).

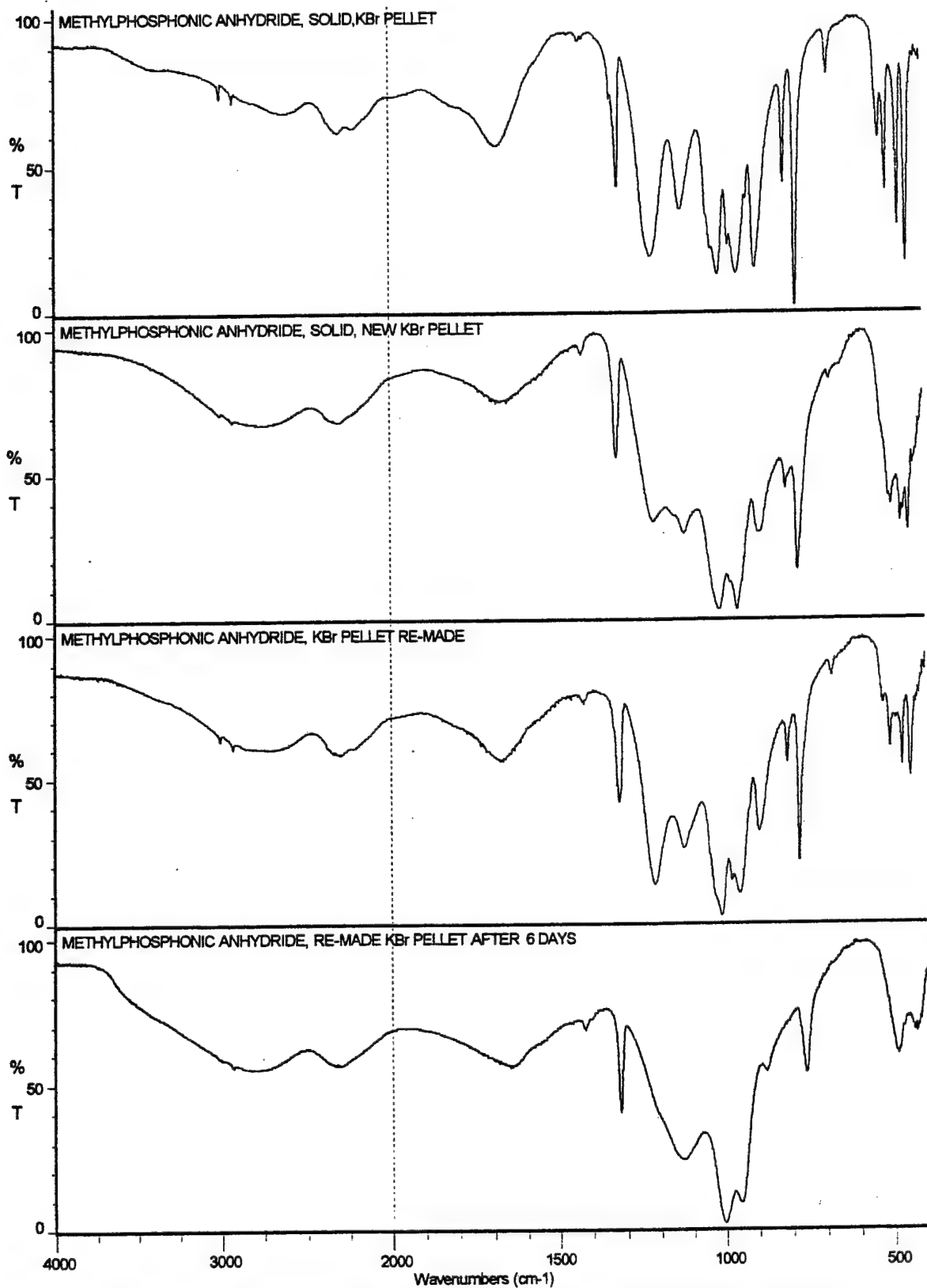
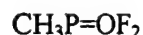


Figure 50 EFFECT OF GRINDING ON THE METHYLPHOSPHONIC ANHYDRIDE/KBr MATRIX

### 3.3.4 Methylphosphonic Difluoride (DF, Difluor)



The infrared spectrum of methylphosphonic difluoride (DF, Difluor) is given in *Figure 51*. The band assignments are as follows: 3013  $\text{cm}^{-1}$  w and 2937  $\text{cm}^{-1}$  w ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$  P-CH<sub>3</sub>), 1506  $\text{cm}^{-1}$  vw (2 x 755  $\text{cm}^{-1}$  = 1510  $\text{cm}^{-1}$ ), 1418  $\text{cm}^{-1}$  w ( $\delta_{\text{as}}$  P-CH<sub>3</sub>), 1336  $\text{cm}^{-1}$  s ( $\nu$  P=O), 1312  $\text{cm}^{-1}$  s ( $\delta_{\text{sy}}$  P-CH<sub>3</sub>), 944  $\text{cm}^{-1}$  sh and 926  $\text{cm}^{-1}$  s (P-CH<sub>3</sub> rock), 882  $\text{cm}^{-1}$  ms and 857  $\text{cm}^{-1}$  m ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$  PF<sub>2</sub>), 755  $\text{cm}^{-1}$  m ( $\nu$  P-C), 469  $\text{cm}^{-1}$  ms (PF<sub>2</sub> deformation ?), 415 and 407  $\text{cm}^{-1}$  m (P=O deformation, PF<sub>2</sub> deformation ?).

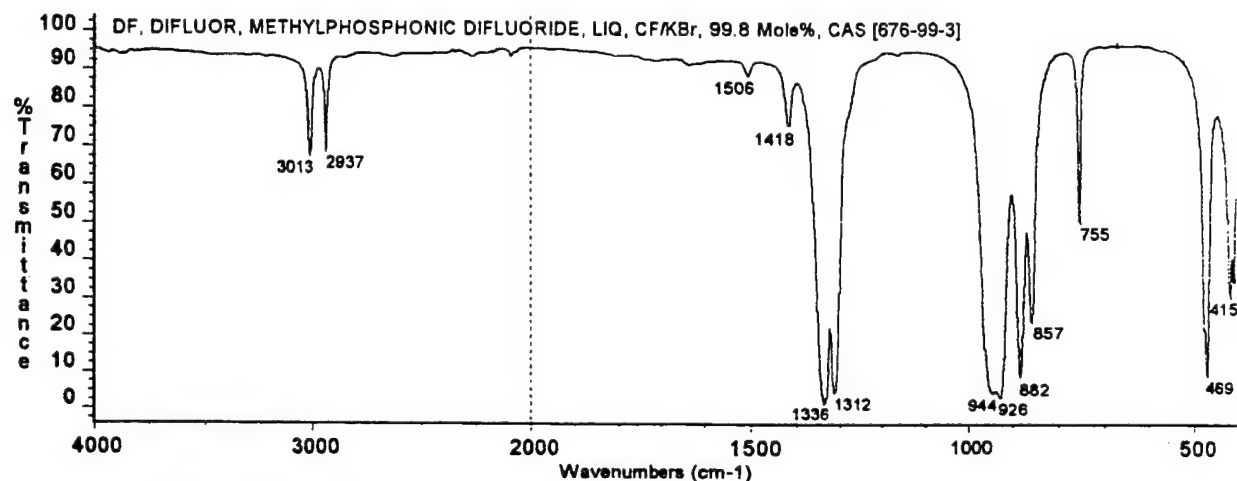


Figure 51 METHYLPHOSPHONIC DIFLUORIDE (DF, DIFLUOR), 99.8 MOLE%, LIQUID, CF/KBr

The effect of atmospheric moisture on the infrared spectrum of a thin liquid film of Difluor between KBr windows is given in *Figures 52A* through *52E*. The infrared spectrum for a typical munition sample of Difluor (somewhat dark in color) is given in *Figure 52A*. The presence of an acid moiety is

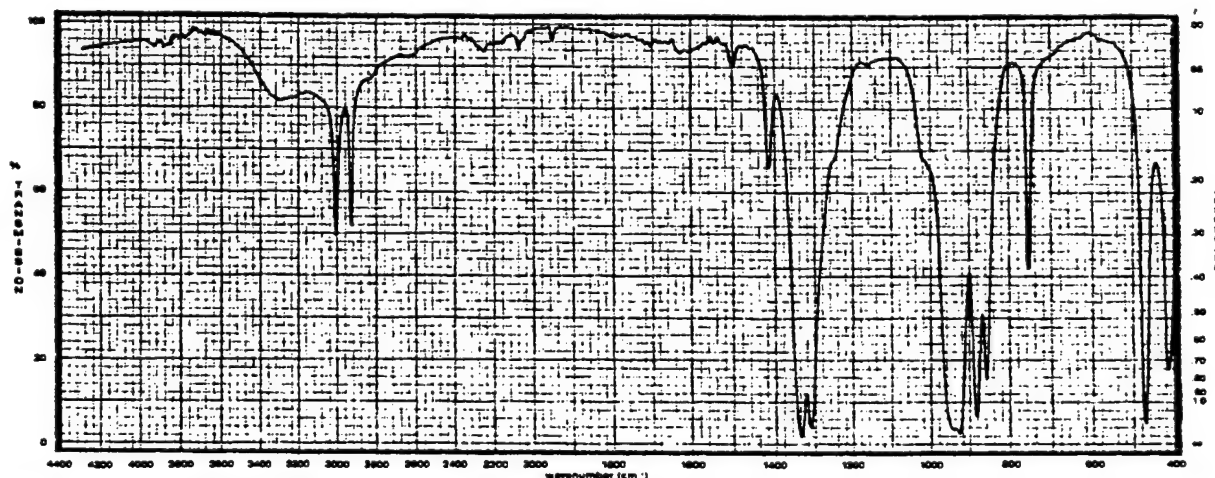


Figure 52A DIFLUOR, LIQUID (SOMEWHAT DARK), CF/KBr

evidenced by the inflections occurring near  $1260\text{ cm}^{-1}$  ( $\nu\text{ P=O}$ ) and  $1020\text{ cm}^{-1}$  ( $\nu\text{ P-OH}$ ). There is also some broadening of the area around  $3000\text{ cm}^{-1}$  (POH) and some absorption is evident near  $3300\text{ cm}^{-1}$  ( $\text{H}_2\text{O}$ ). The sample, after sitting in the air for 30 minutes, *Figure 52B*, shows bands in the 3000 and 2300  $\text{cm}^{-1}$  areas as well as those near 1260 and  $1020\text{ cm}^{-1}$  beginning to become more predominant. The sample of Difluor is beginning to undergo hydrolysis to the Fluoro Acid, methylphosphonofluoridic acid ( $\text{CH}_3\text{P=O(OH)(F)}$ ). This is even more evident after 120 minutes (*Figure 52C*). After an atmospheric

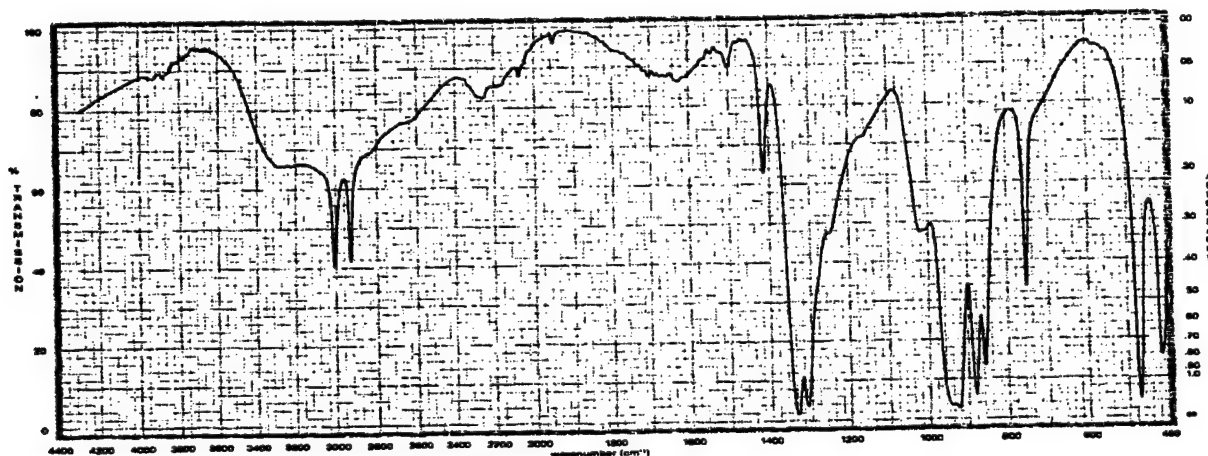


Figure 52B DIFLUOR, LIQUID, CF/KBr, AFTER 30 MINUTES

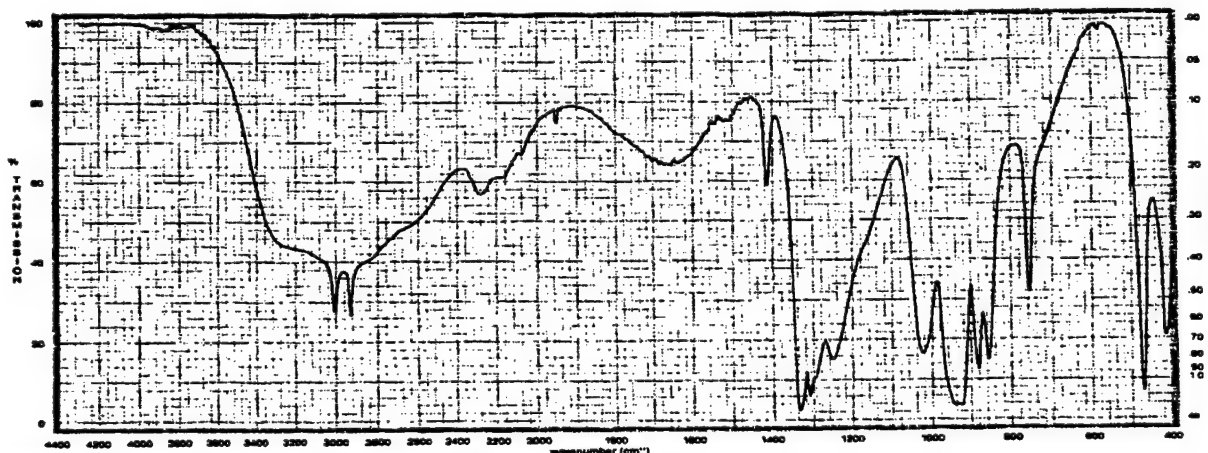


Figure 52C DIFLUOR, LIQUID, CF/KBr, AFTER 120 MINUTES

exposure of 120 minutes, the sample shows more intense bands near 3000, 2300 and  $1650\text{ cm}^{-1}$  due to the POH group. Bands near  $1230\text{ cm}^{-1}$  ( $\nu\text{ P=O}$ ) and  $1020\text{ cm}^{-1}$  ( $\nu\text{ P-OH}$ ) indicate the formation of a P-acid, namely the Fluoro Acid. After a period of 330 minutes, the infrared spectrum (*Figure 52D*) showed

mainly the presence of methylphosphonofluoridic acid (**Fluoro Acid**). The infrared spectrum for an

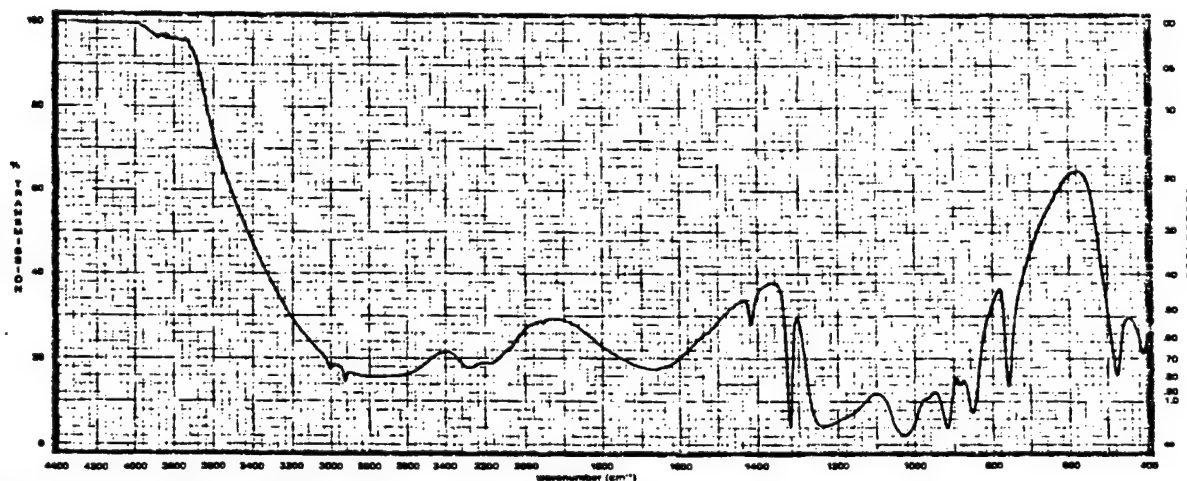


Figure 52D DIFLUOR, LIQUID, CF/KBr, AFTER 330 MINUTES

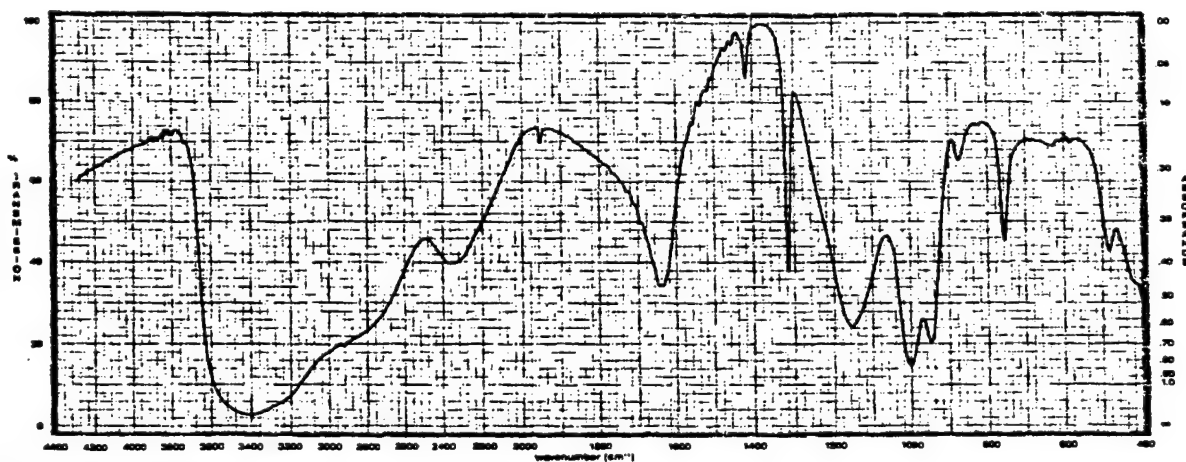


Figure 52E DIFLUOR, LIQUID, CF/KBr, AFTER 71 HOURS

authentic sample of the **Fluoro Acid** is given in *Figure 53*. The infrared spectrum for the sample of **Difluor**, after 71 hours of atmospheric exposure, is reproduced as *Figure 52E*. Here the sample of methylphosphonic difluoride has been hydrolyzed to a very wet methylphosphonic acid (MPA),  $\text{CH}_3\text{P}=\text{O}(\text{OH})_2$ . An authentic spectrum of *wet MPA* is given in *Figure 54*. Thus, the hydrolysis of **Difluor** may be summarized as follows:



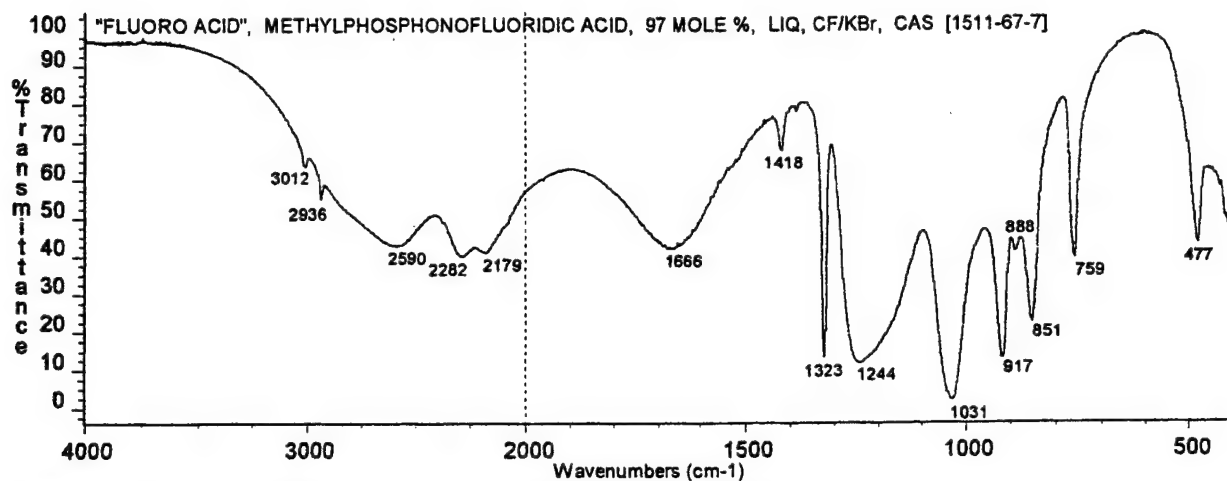


Figure 53 METHYLPHOSPHONOFUORIDIC ACID (FLUORO ACID), LIQUID, CF/KBr

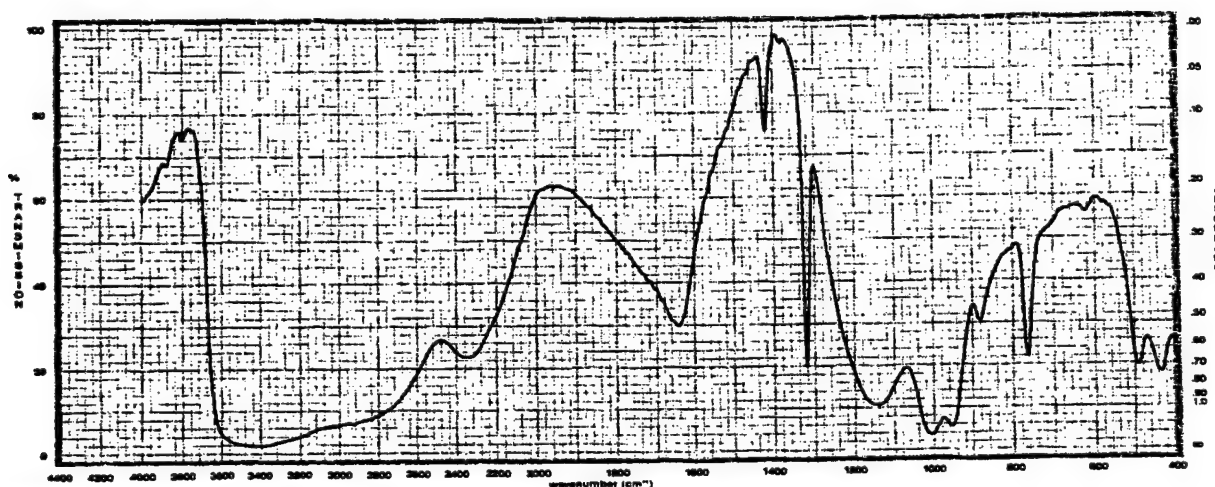
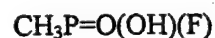


Figure 54 MIX OF A DROP OF WATER AND METHYLPHOSPHONIC ACID (MPA), CF/KBr

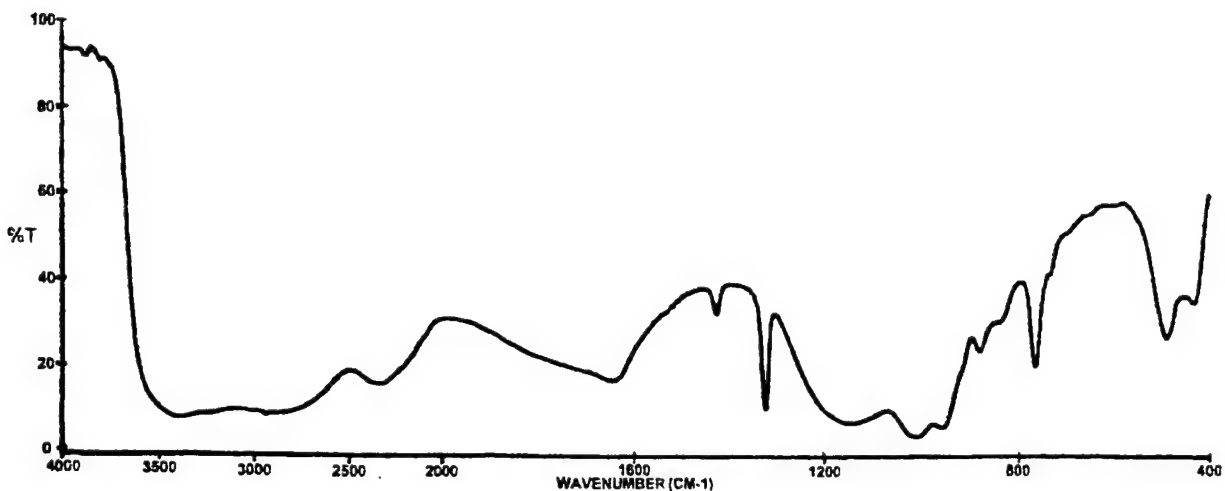
### 3.3.5 Methylphosphonofluoridic Acid (Fluoro Acid)



The infrared spectrum of methylphosphonofluoridic acid (**Fluoro acid**) is given in *Figure 53*.

Band assignments are as follows: 3012 cm<sup>-1</sup> vw and 2936 vw cm<sup>-1</sup> (ν<sub>as</sub> and ν<sub>sy</sub> CH<sub>3</sub>), 2590 cm<sup>-1</sup>, 2282 cm<sup>-1</sup>, 2179 cm<sup>-1</sup> and 1666 cm<sup>-1</sup> (all w-m and broad, POH), 1418 cm<sup>-1</sup> vw (δ<sub>as</sub> P-CH<sub>3</sub>), 1384 cm<sup>-1</sup> vvw (KNO<sub>3</sub> from the KBr windows), 1323 cm<sup>-1</sup> ms (δ<sub>sy</sub> P-CH<sub>3</sub>), 1244 cm<sup>-1</sup> ms, somewhat broadened (ν P=O), 1031 cm<sup>-1</sup> s (ν P-OH), 917 cm<sup>-1</sup> ms (P-CH<sub>3</sub> rock), 851 cm<sup>-1</sup> m (ν P-F), 759 cm<sup>-1</sup> w (ν P-C), 477 cm<sup>-1</sup> w (P=O deformation ?).

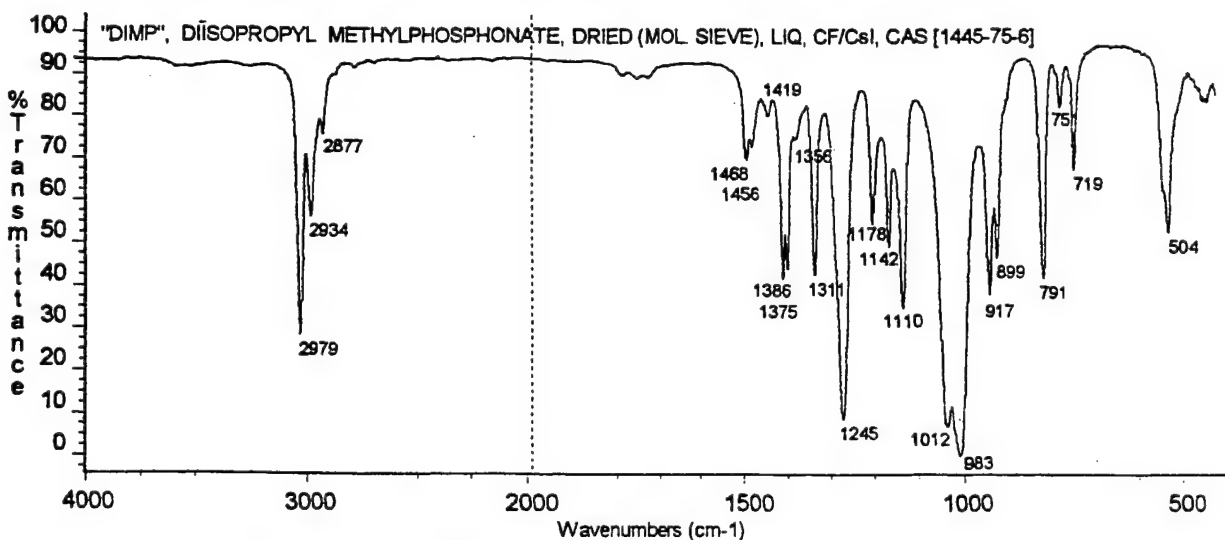
The effect of atmospheric moisture on **Fluoro acid**, after 18 hours of exposure to atmospheric moisture, is shown in **Figure 55**. The P-F stretching band that was at  $851\text{ cm}^{-1}$ , has been almost completely hydrolyzed off leaving a OH group in its place. The resultant compound is methylphosphonic acid, MPA,  $\text{CH}_3\text{P}=\text{O}(\text{OH})_2$ . Compare this spectrum with that for MPA (**Figure 54**).



**Figure 55** FLUORO ACID, LIQ, CF/KBr, AFTER 18 HOURS EXPOSED TO ATMOSPHERIC MOISTURE

### 3.3.6 Diisopropyl Methylphosphonate (DIMP) $\text{CH}_3\text{P}=\text{O}[\text{O}-\text{CH}(\text{CH}_3)_2]_2$

The infrared spectrum of diisopropyl methylphosphonate (**DIMP**) is presented in **Figure 56**. The band assignments are as follows:  $2979\text{ cm}^{-1}$  m,  $2934\text{ cm}^{-1}$  w and  $2877\text{ cm}^{-1}$  vw ( $\nu\text{ CH}_3$ ),  $1468\text{ cm}^{-1}$  and

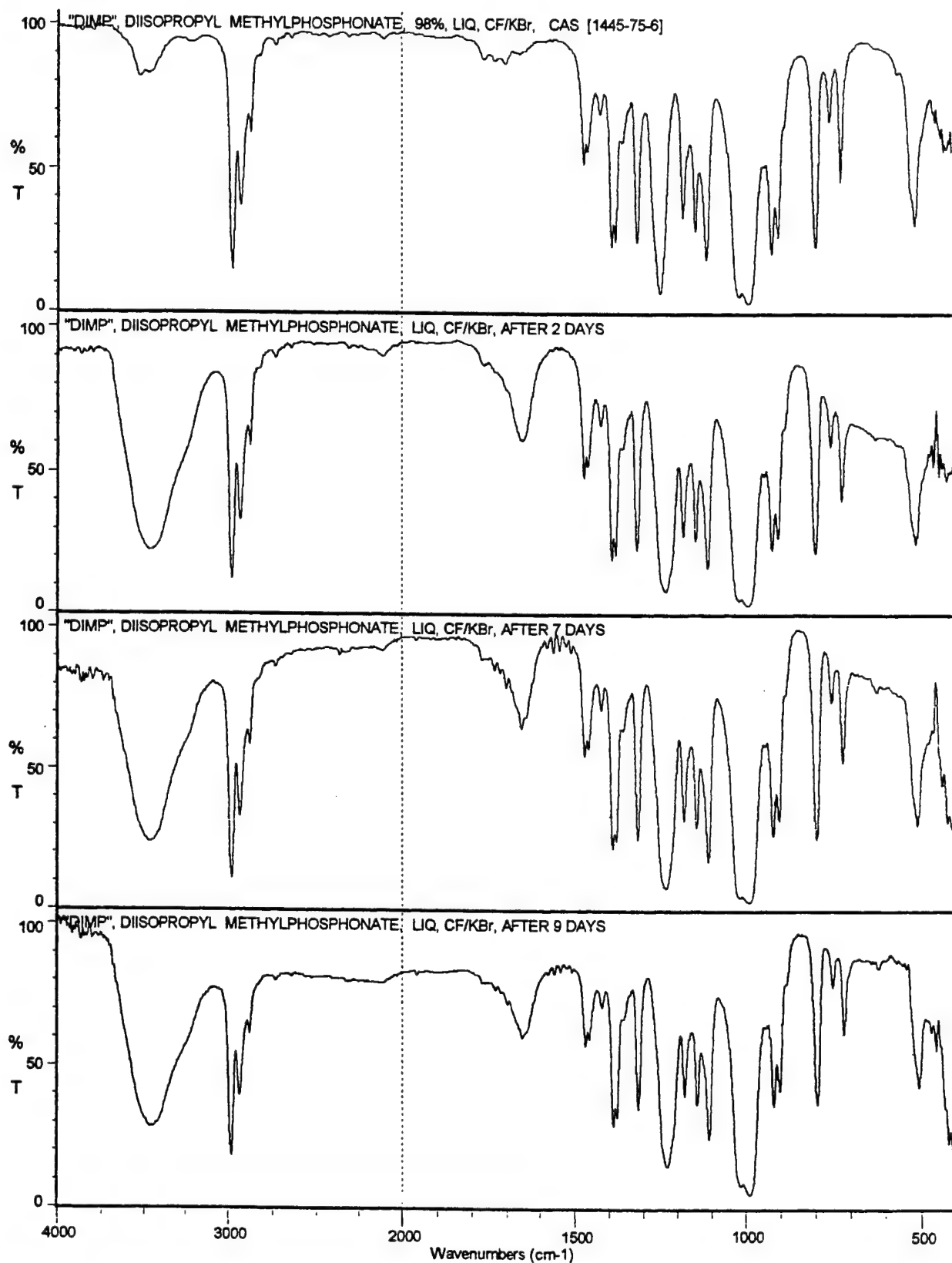


**Figure 56** DIISOPROPYL METHYLPHOSPHONATE (DIMP), DRIED, CF/CsI



1458  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$   $\text{CH}_3$ ), 1419  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$   $\text{P-CH}_3$ ), 1386 and 1375  $\text{cm}^{-1}$  medium (doublet,  $\delta_{\text{sy}}$   $\text{CH}_3$  isopropyl group), 1356  $\text{cm}^{-1}$  sh ( $\delta$  -CH), 1311  $\text{cm}^{-1}$  m ( $\delta_{\text{sy}}$   $\text{P-CH}_3$ ), 1245  $\text{cm}^{-1}$  ms ( $\nu$   $\text{P=O}$ ), 1178  $\text{cm}^{-1}$  w, 1142  $\text{cm}^{-1}$  w and 1110  $\text{cm}^{-1}$  m (triplet of bands characteristic of  $\text{P-O-isopropyl}$ ), 1012  $\text{cm}^{-1}$  sh and 983  $\text{cm}^{-1}$  s ( $\nu$   $\text{P-O-C}$ ), 917  $\text{cm}^{-1}$  m and 899  $\text{cm}^{-1}$  w ( $\text{CH}_3$  rock of  $\text{P-CH}_3$  and isopropyl groups), 791  $\text{cm}^{-1}$  m (POC), 719  $\text{cm}^{-1}$  w ( $\nu$   $\text{P-C}$ ), 504  $\text{cm}^{-1}$  m ( $\text{P=O}$  deformation ?).

The effect of atmospheric moisture on the infrared spectrum of diisopropyl methylphosphonate (DIMP) is illustrated by *Figure 57*. As the amount of water increases, as indicated by the bands near 3465  $\text{cm}^{-1}$  and 1650  $\text{cm}^{-1}$ , the  $\text{P=O}$  stretching band at 1245  $\text{cm}^{-1}$  decreases in value to 1230  $\text{cm}^{-1}$  by the 9<sup>th</sup> day. This lowering of the phosphoryl stretching band by water is due to hydrogen bonding.



**Figure 57** EFFECT OF ATMOSPHERIC MOISTURE ON DIISOPROPYL METHYLPHOSPHONATE (DIMP), LIQUID, CF/KBr

### 3.3.7 2-Propanol (Isopropyl Alcohol, Isopropanol)



The infrared spectrum of 2-propanol (isopropyl alcohol) is reproduced in *Figure 58*. The band assignments are as follows: 3350  $\text{cm}^{-1}$  ms ( $\nu$  OH bonded), 2972  $\text{cm}^{-1}$  s, 2932  $\text{cm}^{-1}$  m and 2884  $\text{cm}^{-1}$  m ( $\nu$   $\text{CH}_3$ ), 1468  $\text{cm}^{-1}$  m ( $\delta_{\text{as}}$   $\text{CH}_3$ ), 1409  $\text{cm}^{-1}$  w ( $\beta$  OH), 1380  $\text{cm}^{-1}$  m and 1368  $\text{cm}^{-1}$  sh ( $\delta_{\text{sy}}$   $\text{CH}_3$ ), 1341  $\text{cm}^{-1}$  w ( $\delta$  -CH), 1310  $\text{cm}^{-1}$  m (CH wag), 1162  $\text{cm}^{-1}$  m, 1130  $\text{cm}^{-1}$  m and 1111  $\text{cm}^{-1}$  sh (isopropyl skeletal and  $\nu_{\text{out-of-phase}}$  C-C-O), 953  $\text{cm}^{-1}$  s (isopropyl moiety,  $\text{CH}_3$  rock), 817  $\text{cm}^{-1}$  m ( $\nu_{\text{in-phase}}$  C-C-O), 669  $\text{cm}^{-1}$  w broad ( $\gamma$  OH).

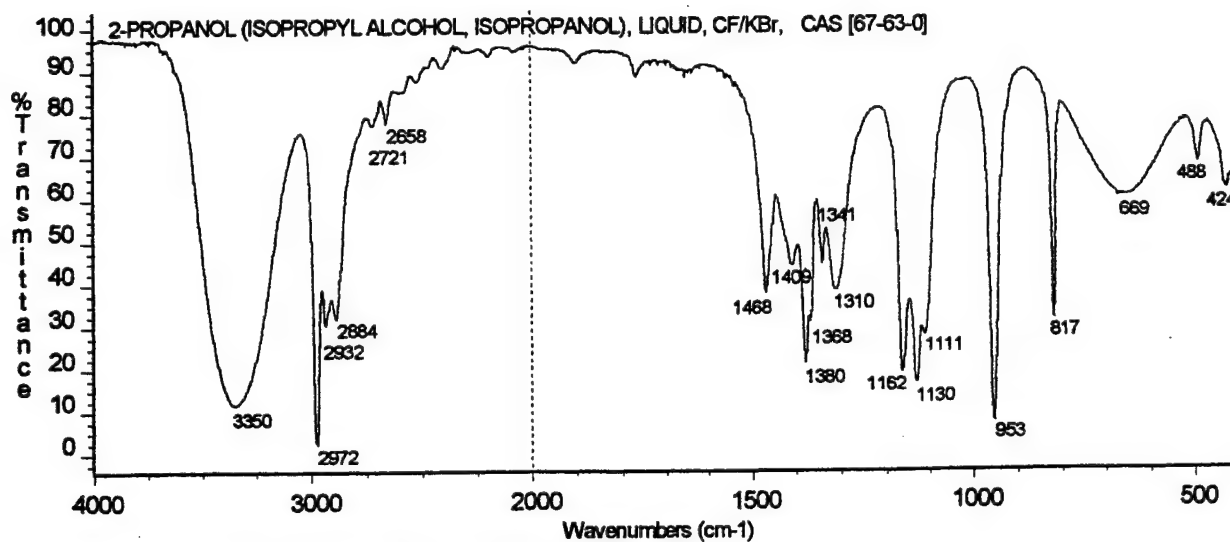


Figure 58 2-PROPANOL (ISOPROPYL ALCOHOL), LIQUID, CF/KBr

### 3.3.8 Cyclohexyl Methylphosphonic Acid (GF Acid)



The infrared spectrum of GF acid, cyclohexyl methylphosphonic acid (or cyclohexyl hydrogen methylphosphonate) is given in *Figure 59*. The band assignments are as follows: 2937  $\text{cm}^{-1}$  ms ( $\nu_{\text{as}}$   $\text{CH}_2$ ), 2860  $\text{cm}^{-1}$  m ( $\nu_{\text{sy}}$   $\text{CH}_2$ ), 2661, 2292 and 1670  $\text{cm}^{-1}$  all weak and broad (POH), 1452  $\text{cm}^{-1}$  w (ring  $\delta$   $\text{CH}_2$ ), 1419  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ), 1313  $\text{cm}^{-1}$  w ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ), 1202  $\text{cm}^{-1}$  ms ( $\nu$  P=O), 1042  $\text{cm}^{-1}$  sh and 1007  $\text{cm}^{-1}$  s ( $\nu$  P-O-C), 909  $\text{cm}^{-1}$  w (P- $\text{CH}_3$  rock), 762  $\text{cm}^{-1}$  w (POC).

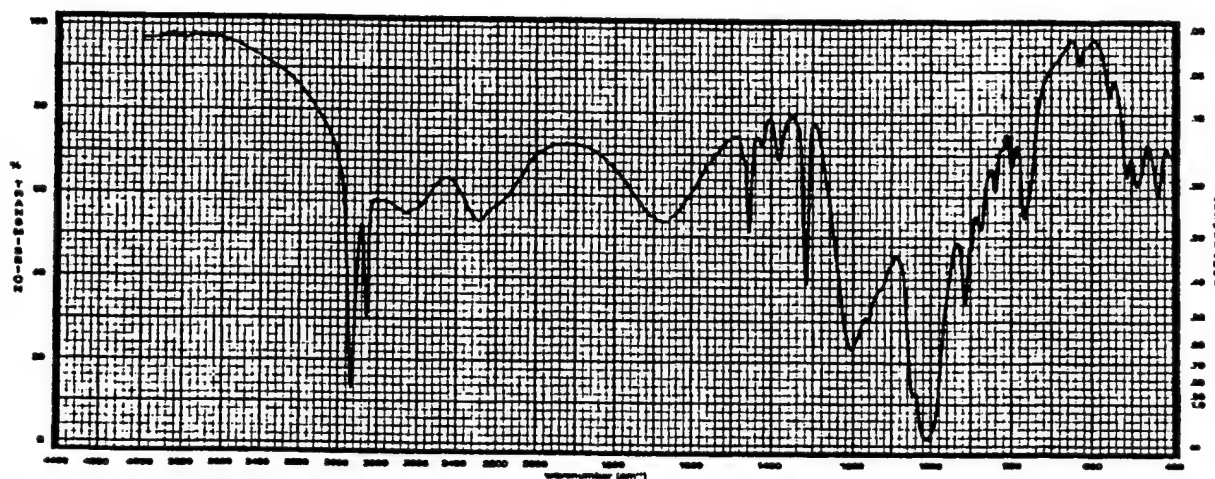


Figure 59 CYCLOHEXYL METHYLPHOSPHONIC ACID (GF ACID), LIQUID, CF/KBr

### 3.3.9 Pinacolyl Methylphosphonic Acid (GD Acid) $\text{CH}_3\text{P}=\text{O}(\text{OH})[\text{O}-\text{CH}(\text{CH}_3)-\text{C}(\text{CH}_3)_3]$

The infrared spectrum of **GD acid**, pinacolyl methylphosphonic acid (pinacolyl hydrogen methylphosphonate or 1,2,2-trimethylpropyl hydrogen methylphosphonate) is given in *Figure 60*.

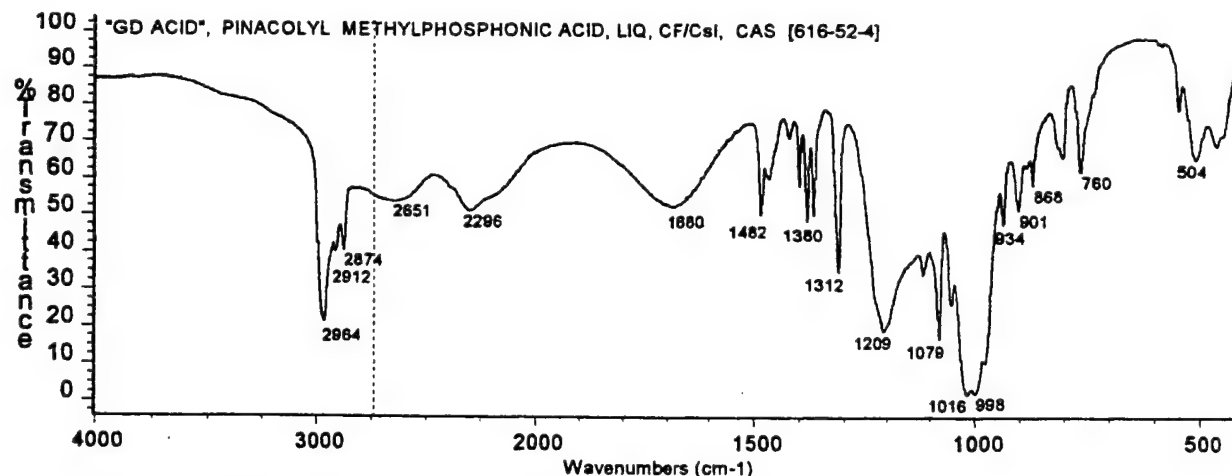


Figure 60 PINACOLYL METHYLPHOSPHONIC ACID (GD ACID), LIQUID, CF/CsI

The band assignments for **GD acid** are as follows:  $2964\text{ cm}^{-1}$  ms,  $2912\text{ cm}^{-1}$  w and  $2874\text{ cm}^{-1}$  w ( $\nu\text{ CH}_3$ ),  $2651$ ,  $2296$  and  $1680\text{ cm}^{-1}$  all weak and broad (POH),  $1482\text{ cm}^{-1}$  w and  $1464\text{ cm}^{-1}$  vw ( $\delta_{\text{as}}\text{ CH}_3$ ),  $1418\text{ cm}^{-1}$  vvw ( $\delta_{\text{as}}\text{ P-CH}_3$ ),  $1397\text{ cm}^{-1}$  vw and  $1380\text{ cm}^{-1}$  w [ $\delta_{\text{as}}\text{ CH}_3$  from  $\text{C}(\text{CH}_3)_3$ ],  $1366\text{ cm}^{-1}$  w ( $\delta_{\text{sy}}\text{ CH}_3$  from  $\text{C-CH}_3$ ),  $1312\text{ cm}^{-1}$  m ( $\delta_{\text{sy}}\text{ P-CH}_3$ ),  $1209\text{ cm}^{-1}$  ms ( $\nu\text{ P=O}$ ),  $1115\text{ vvw}$ ,  $1079\text{ w}$  and  $1051\text{ w cm}^{-1}$  (pinacolyl moiety),  $1016$  and  $998\text{ cm}^{-1}$  s ( $\nu\text{ P-O-C}$ ),  $976\text{ cm}^{-1}$  ( $\nu\text{ P-OH}$ ),  $934$ ,  $868$  and  $760\text{ cm}^{-1}$  all weak

(pinacolyl moiety),  $901\text{ cm}^{-1}$  w (P-CH<sub>3</sub> rock),  $801\text{ cm}^{-1}$  w (POC ?),  $504\text{ cm}^{-1}$  w (P=O deformation ?).

### 3.3.10 Dipinacolyl Methylphosphonate [bis(1,2,2-Trimethylpropyl) Methylphosphonate]

The infrared spectrum for dipinacolyl methylphosphonate, [bis(1,2,2-trimethylpropyl) methylphosphonate],  $\text{CH}_3\text{P}=\text{O}[\text{O}-\text{CH}(\text{CH}_3)-\text{C}(\text{CH}_3)_3]_2$ , is reproduced in *Figure 61*. The band assignments are as follows: ca  $3530$  and  $3470\text{ cm}^{-1}$  vw (H<sub>2</sub>O),  $2962\text{ cm}^{-1}$  ms,  $2812\text{ cm}^{-1}$  m and  $2874\text{ cm}^{-1}$  m ( $\nu$  CH<sub>3</sub>),  $1481\text{ cm}^{-1}$  m and  $1464\text{ cm}^{-1}$  w ( $\delta_{\text{as}}$  CH<sub>3</sub>),  $1417\text{ cm}^{-1}$  vw ( $\delta_{\text{as}}$  P-CH<sub>3</sub>),  $1396\text{ cm}^{-1}$  w,  $1378\text{ cm}^{-1}$  m and  $1365\text{ cm}^{-1}$  m [ $\delta_{\text{sy}}$  C(CH<sub>3</sub>)<sub>3</sub> and  $\delta_{\text{sy}}$  C-CH<sub>3</sub>],  $1307\text{ cm}^{-1}$  m ( $\delta_{\text{sy}}$  P-CH<sub>3</sub>),  $1248\text{ cm}^{-1}$  ms ( $\nu$  P=O),  $1211\text{ cm}^{-1}$  w [C(CH<sub>3</sub>)<sub>3</sub> ?],  $1115\text{ cm}^{-1}$  w,  $1081\text{ cm}^{-1}$  m,  $1052\text{ cm}^{-1}$  m,  $1021\text{ cm}^{-1}$  ms and  $1006\text{ cm}^{-1}$  ms (pinacolyl moiety),  $971\text{ cm}^{-1}$  s ( $\nu$  P-O-C),  $934\text{ cm}^{-1}$  m (pinacolyl moiety),  $907\text{ cm}^{-1}$  w and  $894\text{ cm}^{-1}$  w [P-CH<sub>3</sub> rock and CH<sub>3</sub> rock of C(CH<sub>3</sub>)<sub>3</sub>],  $867\text{ cm}^{-1}$  w,  $811\text{ cm}^{-1}$  m,  $750\text{ cm}^{-1}$  w,  $723\text{ cm}^{-1}$  vw and  $548\text{ cm}^{-1}$  w (pinacolyl moiety).

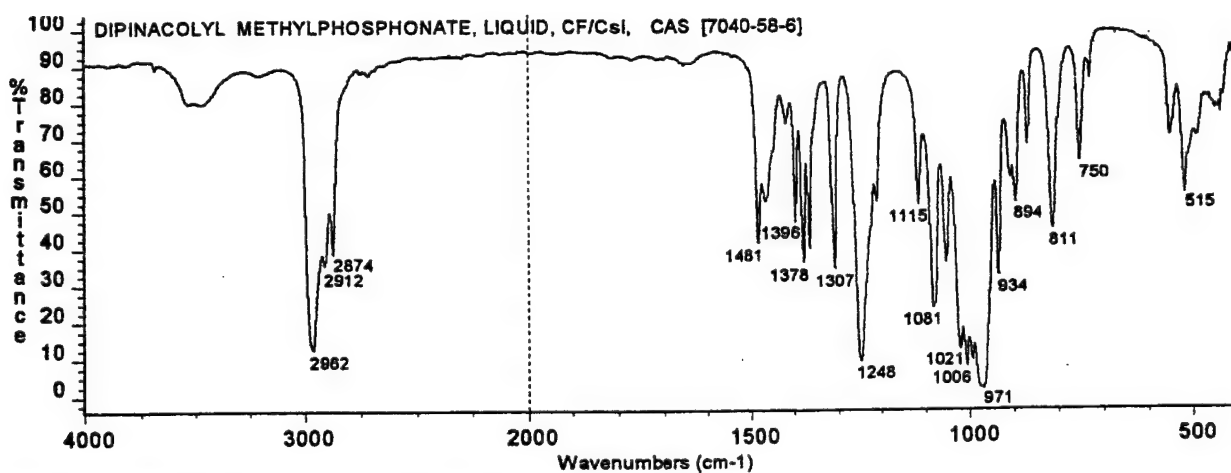


Figure 61 DIPINACOLYL METHYLPHOSPHONATE, LIQUID, CF/CsI

### 3.3.11 Pinacolyl Alcohol (1,2,2-Trimethyl-1-Propanol) $\text{HO}-\text{CH}(\text{CH}_3)-\text{C}(\text{CH}_3)_3$

The infrared spectrum for pinacolyl alcohol (1,2,2-trimethyl-1-propanol or 3,3-dimethyl-2-butanol) is given in *Figure 62*. The band assignments are as follows:  $3393\text{ cm}^{-1}$  ms ( $\nu$  OH bonded),  $2961\text{ cm}^{-1}$  s,  $2909\text{ cm}^{-1}$  m and  $2872\text{ cm}^{-1}$  ms ( $\nu$  CH<sub>3</sub>),  $1480\text{ cm}^{-1}$  m and  $1459\text{ cm}^{-1}$  m ( $\delta_{\text{as}}$  CH<sub>3</sub>),  $1391\text{ w}$  and

1373  $\text{cm}^{-1}$  m ( $\delta_{\text{sy}}$   $\text{CH}_3$  of  $\text{C}(\text{CH}_3)_3$ ), 1364  $\text{cm}^{-1}$  m ( $\delta_{\text{sy}}$   $\text{C}-\text{CH}_3$ ), 1299  $\text{cm}^{-1}$  vw ( $\beta$  OH), 1098 and 1084  $\text{cm}^{-1}$  ms ( $\nu$   $\text{C}-\text{O}$ ), 1201  $\text{cm}^{-1}$  w, 1051  $\text{cm}^{-1}$  m, 1008  $\text{cm}^{-1}$  ms (pinacolyl moiety), 913  $\text{cm}^{-1}$  ms ( $\text{CH}_3$  rock ?), 618  $\text{cm}^{-1}$  w and broad ( $\gamma$  OH).

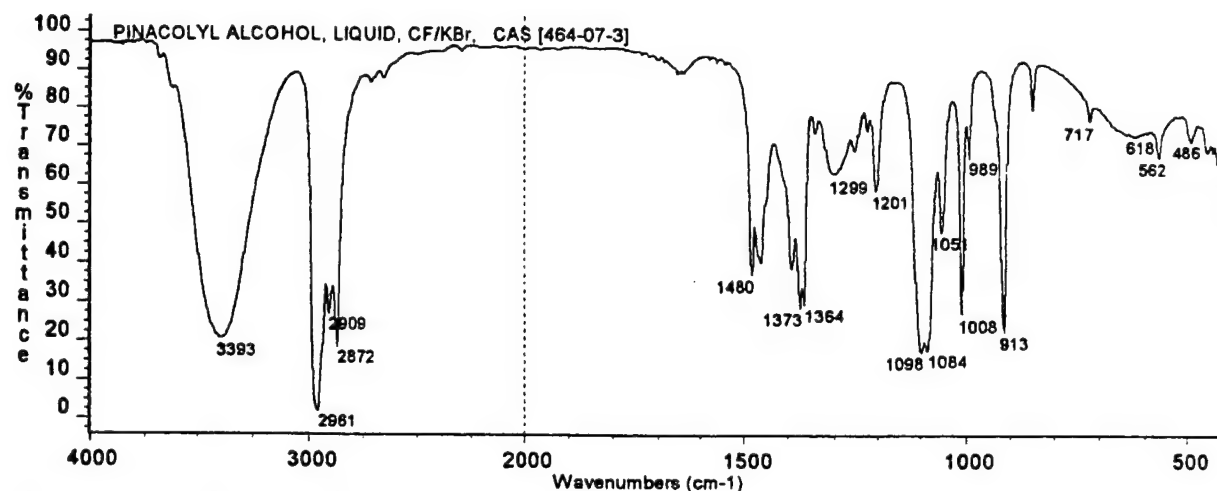


Figure 62 PINACOLYL ALCOHOL (1,2,2-TRIMETHYL-1-PROPANOL), LIQUID, CF/KBr

### 3.3.12 2-Methylcyclohexyl Methylphosphonic Acid (EA 1356 Acid)



The infrared spectrum of 2-methylcyclohexyl methylphosphonic acid (2-methyl-cyclohexyl hydrogen methylphosphonate), EA 1356 Acid, is reproduced in *Figure 63*. The band assignments are as follows: 2931  $\text{cm}^{-1}$  s and 2858  $\text{cm}^{-1}$  ms ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$  and  $\text{CH}_2$ ), 2660  $\text{cm}^{-1}$ , 2296  $\text{cm}^{-1}$  and 1684  $\text{cm}^{-1}$  all weak and broad (POH), 1453  $\text{cm}^{-1}$  w ( $\delta_{\text{as}}$   $\text{CH}_3$  and  $\delta$   $\text{CH}_2$ ), 1419  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$   $\text{P}-\text{CH}_3$ ), 1380  $\text{cm}^{-1}$  vw ( $\delta_{\text{sy}}$   $\text{CH}_3$ ), 1311  $\text{cm}^{-1}$  m ( $\delta_{\text{sy}}$   $\text{P}-\text{CH}_3$ ), 1053  $\text{cm}^{-1}$  sh and 954  $\text{cm}^{-1}$  sh (cyclohexyl ring ?), 1001  $\text{cm}^{-1}$  s ( $\nu$   $\text{P}-\text{O}-\text{C}$  and also  $\nu$   $\text{P}-\text{OH}$ , possible shoulder at 987  $\text{cm}^{-1}$  ?), 904  $\text{cm}^{-1}$  m ( $\text{P}-\text{CH}_3$  rock), 760  $\text{cm}^{-1}$  m (POC), 496  $\text{cm}^{-1}$  w ( $\text{P}=\text{O}$  deformation ?).

### 3.3.13 Monosodium Salt of Methylphosphonic Acid (NAMPA) $\text{CH}_3\text{P}=\text{O}(\text{ONa})(\text{OH})$

The infrared spectrum of the monosodium salt of methylphosphonic acid (NAMPA) is given in *Figure 64*. The band assignments for the dried sample are as follows: 3378  $\text{cm}^{-1}$  w, 3283  $\text{cm}^{-1}$  vw and

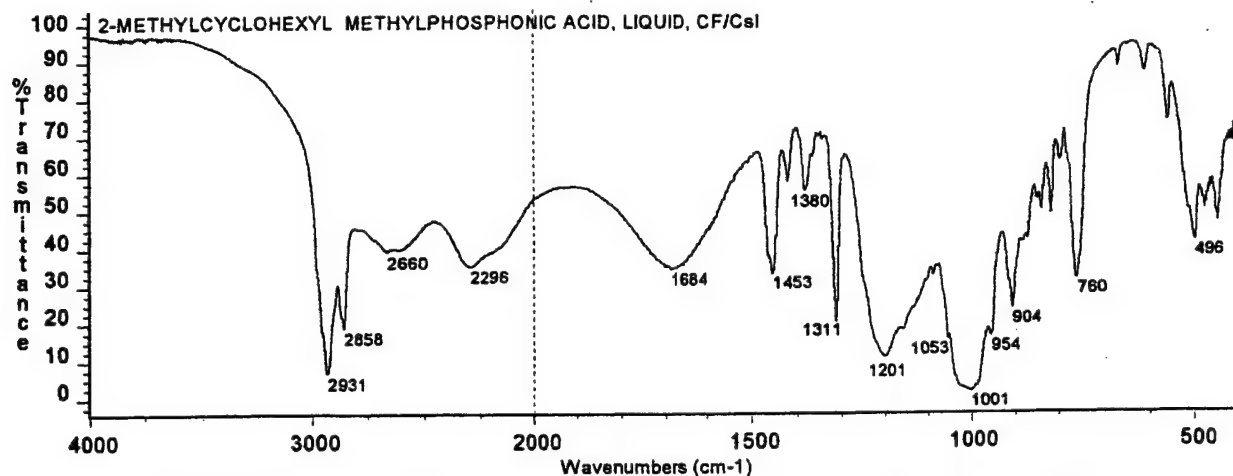


Figure 63 2-METHYLCYCLOHEXYL METHYLPHOSPHONIC ACID (EA 1356 ACID), LIQUID, CF/CsI

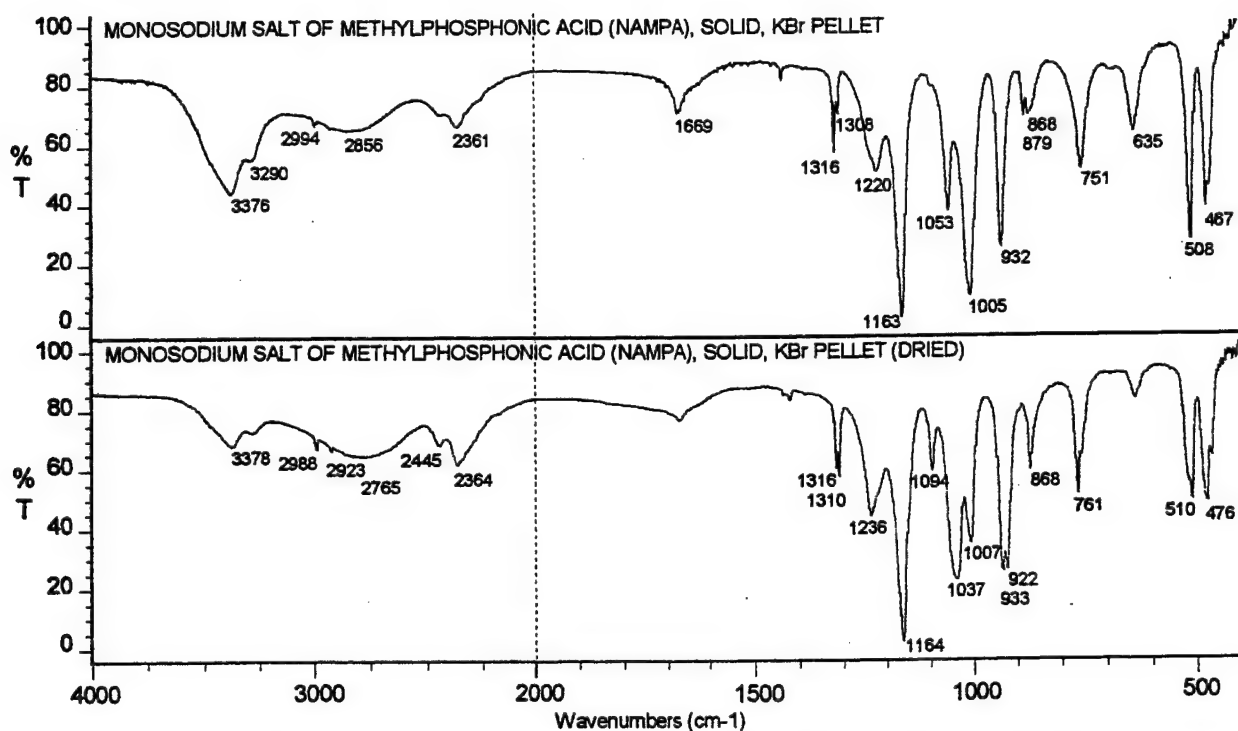


Figure 64 MONOSODIUM SALT OF METHYLPHOSPHONIC ACID (NAMPa), SOLID, KBr PELLET  
Upper Spectrum WET SAMPLE  
Lower Spectrum DRIER SAMPLE

1669  $\text{cm}^{-1}$  vw ( $\text{H}_2\text{O}$ ), 2988  $\text{cm}^{-1}$  vw and 2923  $\text{cm}^{-1}$  vw ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$ ), 2765  $\text{cm}^{-1}$  w, 2445  $\text{cm}^{-1}$  vw, 2364  $\text{cm}^{-1}$  w, and ca 1700  $\text{cm}^{-1}$  vw (POH), 1419  $\text{cm}^{-1}$  vvw ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ), 1316 and 1310  $\text{cm}^{-1}$  w ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ), 1164  $\text{cm}^{-1}$  s ( $\nu_{\text{as}}$   $\text{PO}_2^-$ ), 1037  $\text{cm}^{-1}$  m ( $\nu_{\text{sy}}$   $\text{PO}_2^-$ ), 1007  $\text{cm}^{-1}$  m ( $\nu$  P-OH), 933  $\text{cm}^{-1}$  and 922  $\text{cm}^{-1}$  m

(P-CH<sub>3</sub> rock), 761 cm<sup>-1</sup> w (ν P-C), 510 and 476 cm<sup>-1</sup> m (PO<sub>2</sub><sup>-</sup> deformation). Notice the difference in band intensities and band positions between the wet and dried samples. The only difference between these two samples was the KBr pellet from the upper spectrum in *Figure 64* was allowed to remain in the dry instrument purge for 15 days. The pellet was re-scanned and thus became the lower spectrum labeled 'drier'.

### 3.3.14 Disodium Methylphosphonate (Na<sub>2</sub>MP) <sup>c</sup> CH<sub>3</sub>P=O(O<sup>-</sup>Na<sup>+</sup>)<sub>2</sub>

The infrared spectrum of disodium methylphosphonate, Na<sub>2</sub>MP, is given in *Figure 65*. This figure shows the compound, as a KBr pellet, after various levels of drying time. Band assignments for the KBr pellet as originally prepared are as follows: 3285 ms, 3147 ms, 2333 w and 1701 vw cm<sup>-1</sup> (H<sub>2</sub>O), 2998 cm<sup>-1</sup> vvw (ν CH<sub>3</sub>), 1426 cm<sup>-1</sup> vvw (δ<sub>as</sub> CH<sub>3</sub>), 1313 cm<sup>-1</sup> w (δ<sub>sy</sub> P-CH<sub>3</sub>), 1058 s and 1035 sh cm<sup>-1</sup> (ν<sub>as</sub> PO<sub>3</sub><sup>-</sup>), 976 and 967 cm<sup>-1</sup> m (ν<sub>sy</sub> PO<sub>3</sub><sup>-</sup>), 837 cm<sup>-1</sup> w (P-CH<sub>3</sub> rock ?), 762 cm<sup>-1</sup> m (ν P-C), 526 and 489 w cm<sup>-1</sup> (PO<sub>3</sub><sup>-</sup> deformation).

### 3.3.15 Sodium Isopropyl Methylphosphonate (NAIMP) <sup>c</sup> CH<sub>3</sub>P=O(O<sup>-</sup>Na<sup>+</sup>)[O-CH(CH<sub>3</sub>)<sub>2</sub>]

The infrared spectrum of sodium isopropylmethylphosphonate (NAIMP) is given in *Figure 66*. The band assignments are as follows: 2972 cm<sup>-1</sup> w, 2922 cm<sup>-1</sup> vw and 2871 cm<sup>-1</sup> vvw (ν CH<sub>3</sub>), 1467 cm<sup>-1</sup> vw (δ<sub>as</sub> CH<sub>3</sub>), 1420 cm<sup>-1</sup> vvw (δ<sub>as</sub> P-CH<sub>3</sub>), 1385 and 1370 cm<sup>-1</sup> w (δ<sub>sy</sub> CH<sub>3</sub>), 1297 cm<sup>-1</sup> w (δ<sub>sy</sub> P-CH<sub>3</sub>), 1220 cm<sup>-1</sup> s (ν<sub>as</sub> PO<sub>2</sub><sup>-</sup>), 1177 cm<sup>-1</sup> vw, 1139 cm<sup>-1</sup> vw and 1097 cm<sup>-1</sup> m (characteristic of P-O-isopropyl), 1073 cm<sup>-1</sup> ms (ν<sub>sy</sub> PO<sub>2</sub><sup>-</sup>), 1009 cm<sup>-1</sup> ms (ν P-O-C), 893 cm<sup>-1</sup> m (P-CH<sub>3</sub> rock), 776 cm<sup>-1</sup> m (POC), 720 cm<sup>-1</sup> w (ν P-C), 523 and 500 cm<sup>-1</sup> m (PO<sub>2</sub><sup>-</sup> deformation). The two spectra that make up *Figure 66* again illustrate how moisture effects the resultant spectrum.

<sup>c</sup> These compounds have been discussed previously in Edgewood Arsenal Technical Report EC-TR-76060, "Application of Infrared and Raman Spectroscopy to the Analysis of Phosphonic Acids and Their Salts (GB-Related Compounds), by Piffath, R. J. and Sass, S., June 1976. Approved for public release.



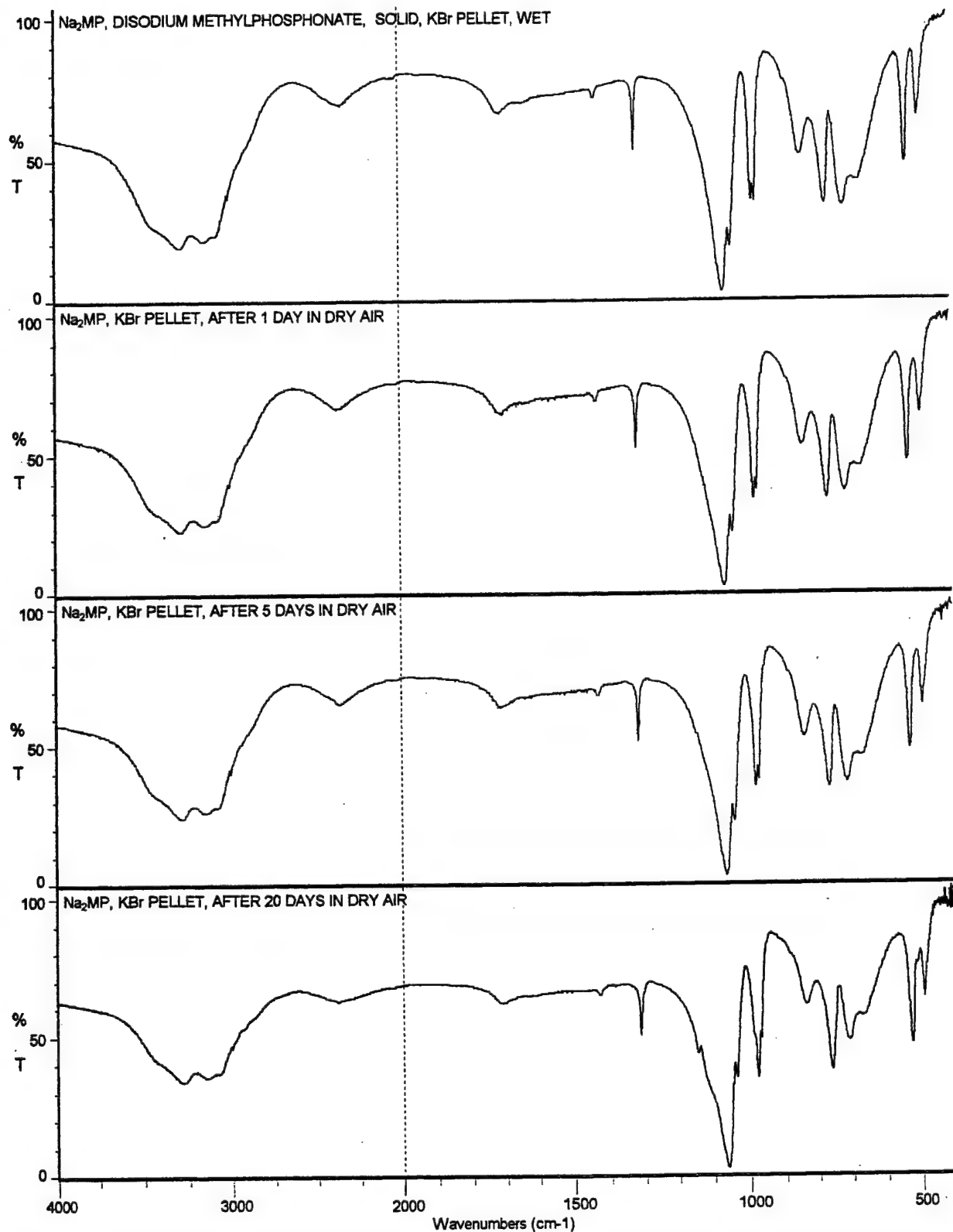


Figure 65 DISODIUM METHYLPHOSPHONATE (Na<sub>2</sub>MP), SOLID, KBr PELLET, AT VARYING DEGREES OF DRYNESS

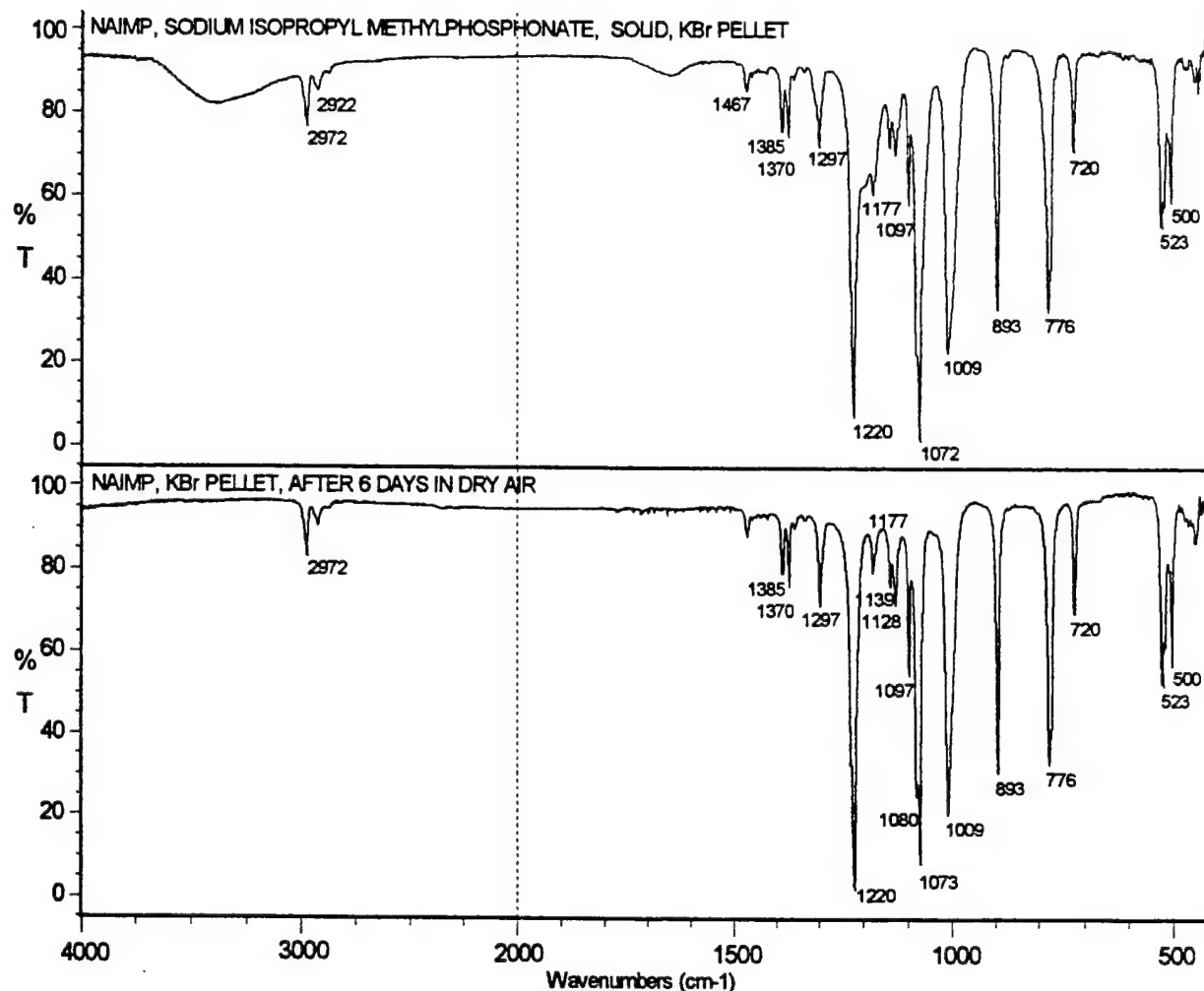
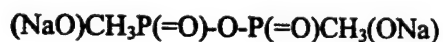


Figure 66 SODIUM ISOPROPYL METHYLPHOSPHONATE (NAIMP), SOLID KBr PELLET  
 UPPER SPECTRUM KBr PELLET AS PREPARED  
 LOWER SPECTRUM KBr PELLET DRIED FOR 6 DAYS

### 3.3.16 Disodium Dimethylpyrophosphonate (NA<sub>2</sub>PYRO)



The infrared spectrum of disodium dimethylpyrophosphonate (NA<sub>2</sub>PYRO) is reproduced in Figure 67. The band assignments are as follows: 3432 cm<sup>-1</sup> w and 1632 cm<sup>-1</sup> vw (H<sub>2</sub>O), 2998 cm<sup>-1</sup> vw and 2933 cm<sup>-1</sup> vw (ν<sub>as</sub> and ν<sub>sy</sub> CH<sub>3</sub>), 1413 cm<sup>-1</sup> vw (δ<sub>as</sub> P-CH<sub>3</sub>), 1304 cm<sup>-1</sup> m (δ<sub>sy</sub> P-CH<sub>3</sub>), 1205 cm<sup>-1</sup> s and 1195 cm<sup>-1</sup> sh (ν<sub>as</sub> PO<sub>2</sub><sup>-</sup>), 1118 cm<sup>-1</sup> ms (ν<sub>sy</sub> PO<sub>2</sub><sup>-</sup>), 968 cm<sup>-1</sup> ms and 942 cm<sup>-1</sup> ms (ν P-O-P), 874 cm<sup>-1</sup> ms (P-CH<sub>3</sub> rock), 785 cm<sup>-1</sup> m and 753 cm<sup>-1</sup> ms (ν P-C), 452 cm<sup>-1</sup> m (PO<sub>2</sub><sup>-</sup> deformation).

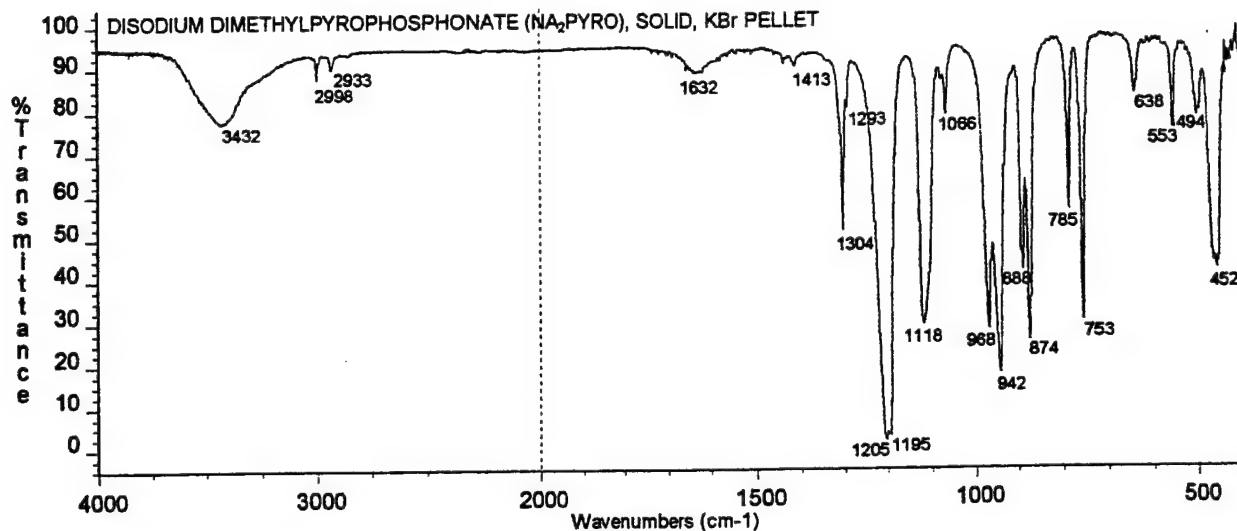


Figure 67 DISODIUM DIMETHYLPYROPHOSPHONATE ( $\text{Na}_2\text{PYRO}$ ), SOLID, KBr PELLET

### 3.4 Precursors of Ethyl N,N-Dimethylphosphoramidocyanidate (GA, Tabun)

Dimethylamine hydrochloride

Phosphorus oxychloride

Dimethylphosphoramidic dichloride

Ethyl phosphorodichloridate

#### 3.4.1 Dimethylamine Hydrochloride $(\text{CH}_3)_2\text{N}\cdot\text{HCl}$

The infrared spectrum of dimethylamine hydrochloride is given in *Figure 68*. Band assignments for the compound are as follows: multiple bands near  $3019\text{ cm}^{-1}$  and  $2770\text{ cm}^{-1}$  are indicative of the  $\nu_{\text{as}}\text{NH}_2^+$  and the  $\nu_{\text{sy}}\text{NH}_2^+$ ,  $2700\text{--}2300\text{ cm}^{-1}$  combination bands  $\text{NH}_2^+$  group,  $1600\text{--}1580\text{ cm}^{-1}$  w-m ( $\delta\text{NH}_2^+$ ),  $1480\text{--}1460\text{ cm}^{-1}$  ms ( $\delta_{\text{as}}\text{N-CH}_3$ ), near  $1420\text{ cm}^{-1}$  m ( $\delta_{\text{sy}}\text{N-CH}_3$ ), near  $1020\text{ cm}^{-1}$  m-s ( $\nu\text{C-N}$ ).

#### 3.4.2 Phosphorus Oxychloride (THO) $\text{POCl}_3$

The infrared spectrum for phosphorus oxychloride (phosphoryl chloride), **THO**,  $\text{POCl}_3$ , is given in *Figure 69*. Band assignments are as follows:  $2585\text{ cm}^{-1}$  vvw ( $2 \times 1298 = 2596\text{ cm}^{-1}$ ),  $1384\text{ cm}^{-1}$  vvw ( $\text{KNO}_3$  from the KBr windows),  $1298\text{ cm}^{-1}$  ms ( $\nu\text{P=O}$ ),  $1180\text{ cm}^{-1}$  vw ( $\nu\text{P=O}$  from the hydrolysis of  $\text{POCl}_3$ ),  $588\text{ cm}^{-1}$  s ( $\nu_{\text{as}}\text{PCl}_3$ ),  $484\text{ cm}^{-1}$  m ( $\nu_{\text{sy}}\text{PCl}_3$ ).

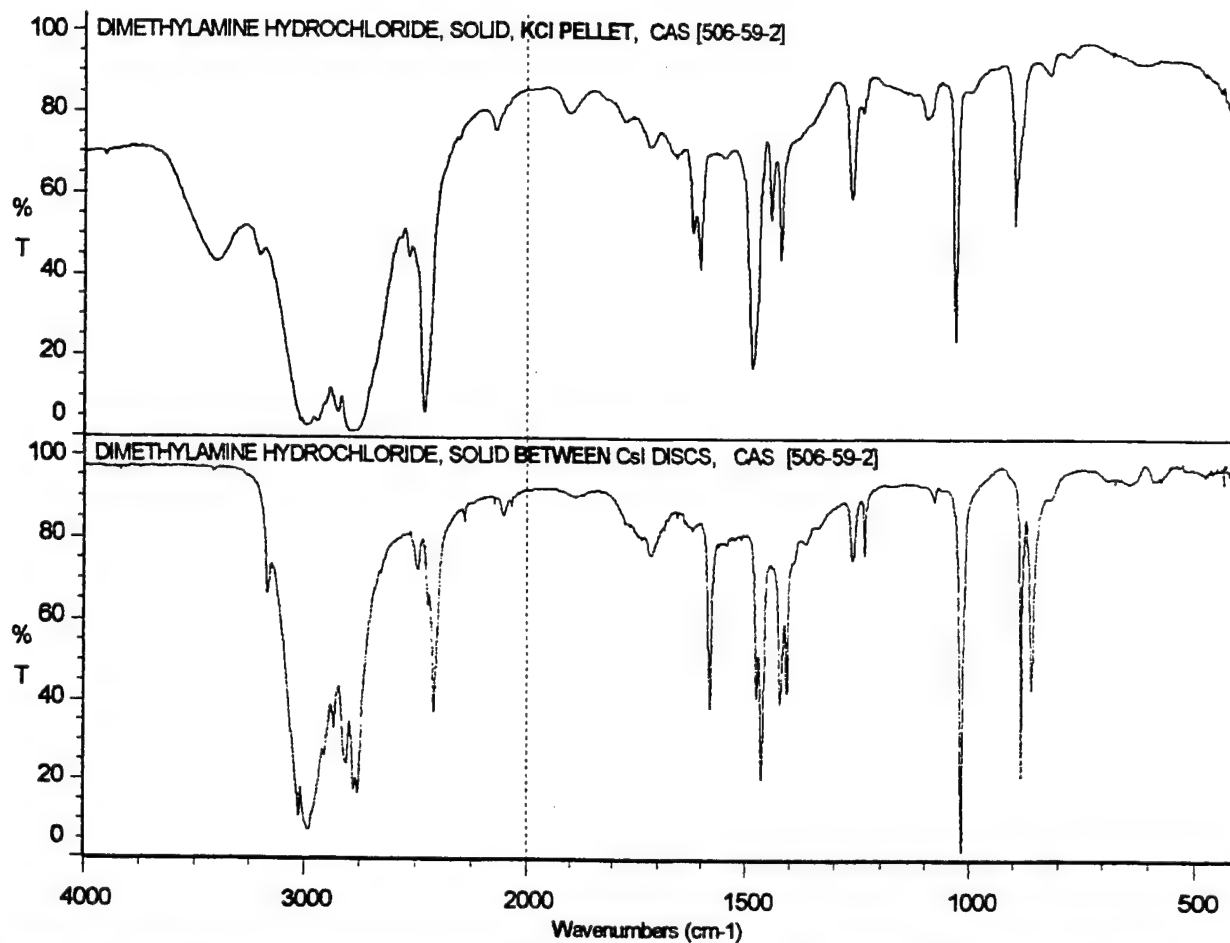


Figure 68 DIMETHYL HYDROCHLORIDE SOLID AS A KCl PELLET (upper spectrum) AND AS A SOLID BETWEEN CsI WINDOWS (lower spectrum)

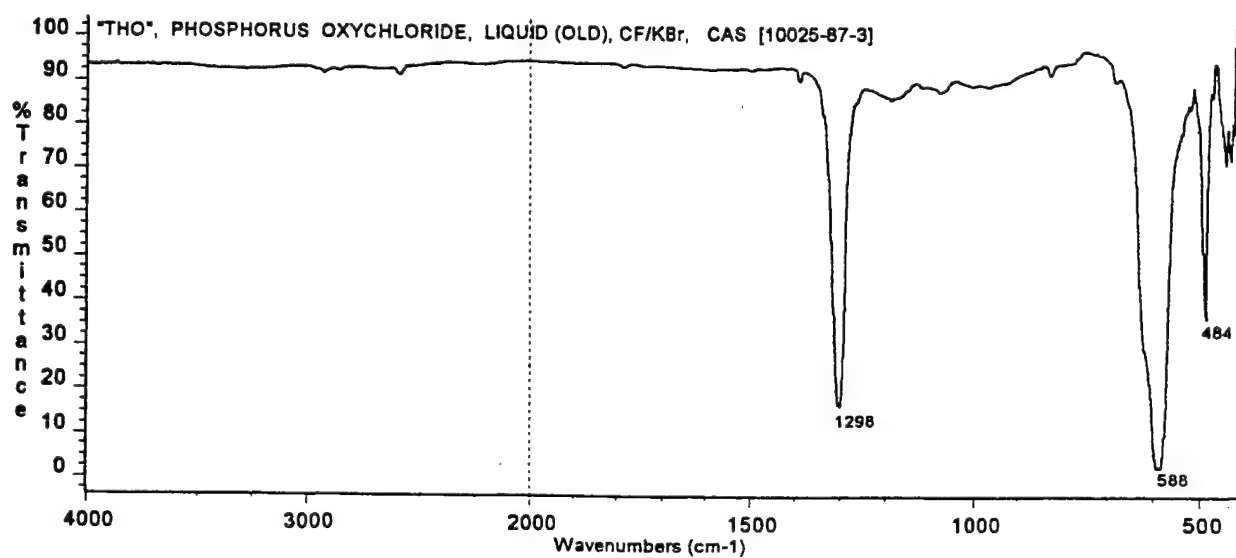
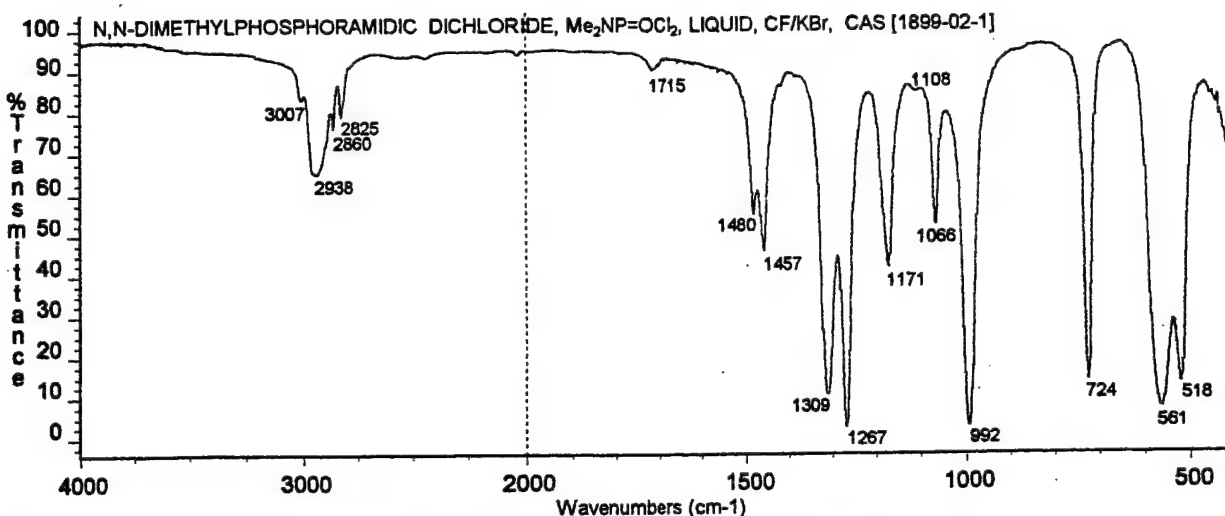


Figure 69 PHOSPHORUS OXYCHLORIDE (THO), LIQUID (OLD), CF/KBr

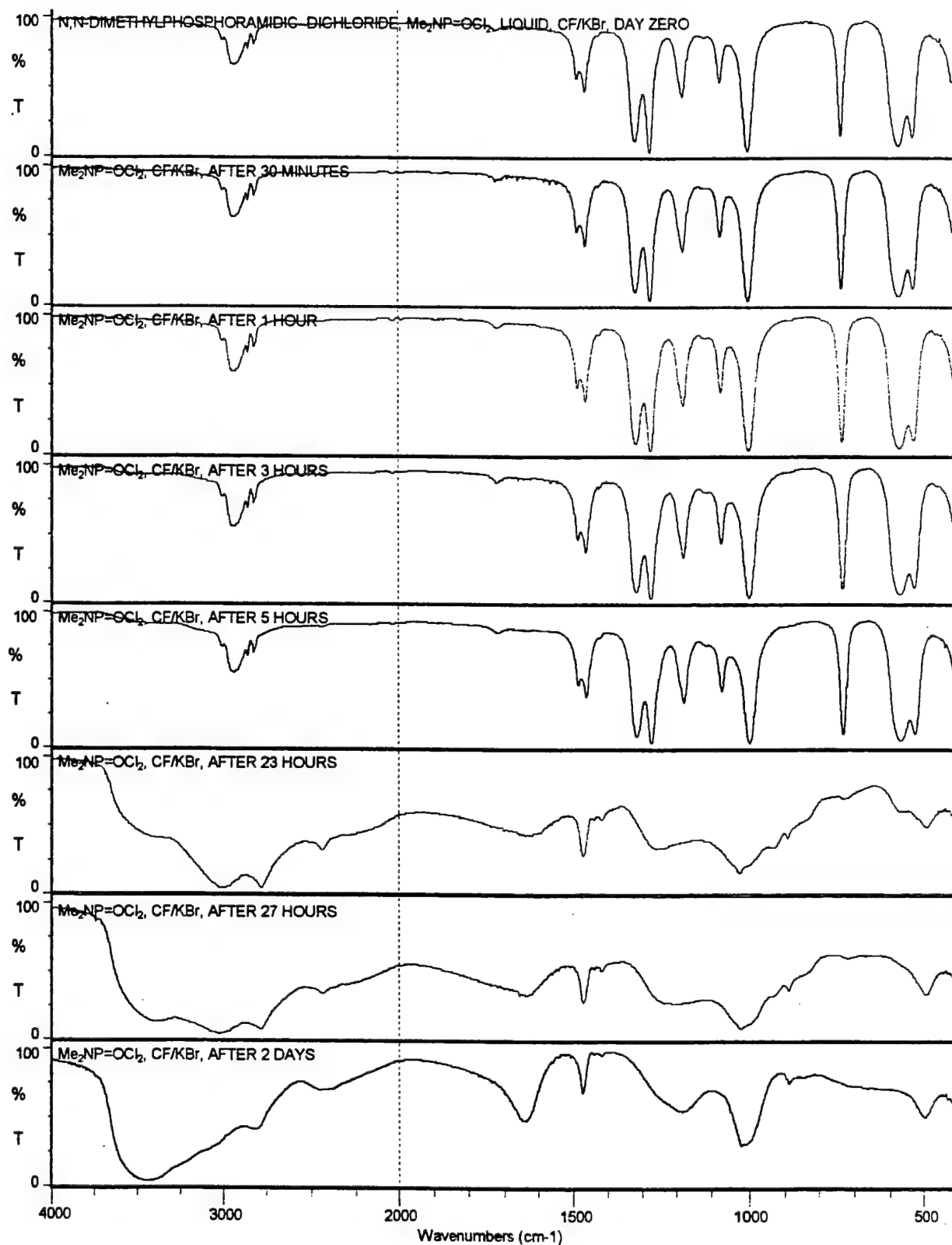
### 3.4.3 N,N-Dimethylphosphoramidic Dichloride $(\text{CH}_3)_2\text{NP}=\text{OCl}_2$

The infrared spectrum of N,N-dimethylphosphoramidic dichloride (dimethylamidophosphoric dichloride) is given in *Figure 70*. The band assignments are as follows:  $3007\text{ cm}^{-1}$  vw,  $2938\text{ cm}^{-1}$  w,  $2860\text{ cm}^{-1}$  vw and  $2825\text{ cm}^{-1}$  vw ( $\nu\text{ CH}_3$ ),  $1715\text{ cm}^{-1}$  vvw ( $992 + 724 = 1716\text{ cm}^{-1}$ ),  $1480\text{ cm}^{-1}$  w and  $1457\text{ cm}^{-1}$  m ( $\delta\text{ CH}_3$ ),  $1309\text{ cm}^{-1}$  ms [ $\text{PN}(\text{CH}_3)_2$ ],  $1267\text{ cm}^{-1}$  s ( $\nu\text{ P}=\text{O}$ ),  $1171\text{ cm}^{-1}$  m and  $1066\text{ cm}^{-1}$  w [ $\text{PN}(\text{CH}_3)_2$ ],  $992\text{ cm}^{-1}$  s ( $\nu_{\text{as}}\text{ P-N-C}$ ),  $724\text{ cm}^{-1}$  ms ( $\nu_{\text{sy}}\text{ P-N-C}$ ),  $561\text{ cm}^{-1}$  ms and  $518\text{ cm}^{-1}$  ms ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}\text{ PCl}_2$ ).



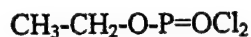
**Figure 70** N,N-DIMETHYLPHOSPHORAMIDIC DICHLORIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on N,N-dimethylphosphoramidic dichloride is shown in *Figure 71*. The compound seems to remain pretty much intact until 5 hours had elapsed. Between the 5 and 23 hour periods the compound hydrolyzes as evidenced by the appearance of strong bands near  $3020$  and  $2780\text{ cm}^{-1}$  and a weak band near  $2439\text{ cm}^{-1}$  indicative of a  $\text{NH}_2^+$  moiety. The bands due to the  $\text{PCl}_2$  group at  $561$  and  $518\text{ cm}^{-1}$  are almost gone from the spectrum as are the bands due to the  $\text{PN}(\text{CH}_3)_2$  group ( $1480, 1457, 1309, 1171, 1066, 992$  and  $724\text{ cm}^{-1}$ ). By day two the remaining material may be a mix of  $\text{HOP}=\text{O}(\text{OH})_2$  and  $(\text{CH}_3)_2\text{NH}$ , perhaps best represented as  $[(\text{HO})_2\text{-PO}_2^-]\text{H}_2\text{N}^+(\text{CH}_3)_2$ .



**Figure 71 EFFECT OF ATMOSPHERIC MOISTURE ON  $N,N$ -DIMETHYLPHOSPHORAMIDIC DICHLORIDE, LIQUID, CF/KBr**

### 3.4.4 Ethyl Phosphorodichloridate



The infrared spectrum of ethyl phosphorodichloridate (ethyl dichlorophosphate) is reproduced as *Figure 72*. Band assignments are as follows: 2990  $\text{cm}^{-1}$  m ( $\nu_{\text{as}}$  CH<sub>3</sub>), 2942  $\text{cm}^{-1}$  w ( $\nu_{\text{as}}$  CH<sub>2</sub>), 2912  $\text{cm}^{-1}$  w ( $\nu_{\text{sy}}$  CH<sub>3</sub>) and 2872  $\text{cm}^{-1}$  vw ( $\nu_{\text{sy}}$  CH<sub>2</sub>), 2594  $\text{cm}^{-1}$  vw ( $1310 + 1295 = 2605 \text{ cm}^{-1}$ ), 1799  $\text{cm}^{-1}$  w ( $1036 + 776 = 1816$ ,  $1013 + 776 = 1789 \text{ cm}^{-1}$ ), 1476  $\text{cm}^{-1}$  m ( $\delta$  OCH<sub>2</sub>), 1445  $\text{cm}^{-1}$  m ( $\delta_{\text{as}}$  CH<sub>3</sub>), 1393  $\text{cm}^{-1}$  m ( $\omega$  OCH<sub>2</sub>), 1371  $\text{cm}^{-1}$  m ( $\delta_{\text{sy}}$  CH<sub>3</sub>), 1310 and 1295  $\text{cm}^{-1}$  s ( $\nu$  P=O doublet, isomers?), 1161  $\text{cm}^{-1}$  m and 1101  $\text{cm}^{-1}$  w (CH<sub>3</sub> rock, characteristic of P-O-ethyl), 1036 and 1013  $\text{cm}^{-1}$  s ( $\nu$  P-O-C), 980  $\text{cm}^{-1}$  ms ( $\nu$  C-C of P-O-ethyl), 776  $\text{cm}^{-1}$  ms (POC), 605  $\text{cm}^{-1}$  sh and 579  $\text{cm}^{-1}$  s ( $\nu_{\text{as}}$  PCl<sub>2</sub> doublet possibly due to isomers), 552  $\text{cm}^{-1}$  sh and 517  $\text{cm}^{-1}$  ms ( $\nu_{\text{sy}}$  PCl<sub>2</sub> doublet possibly due to isomers).

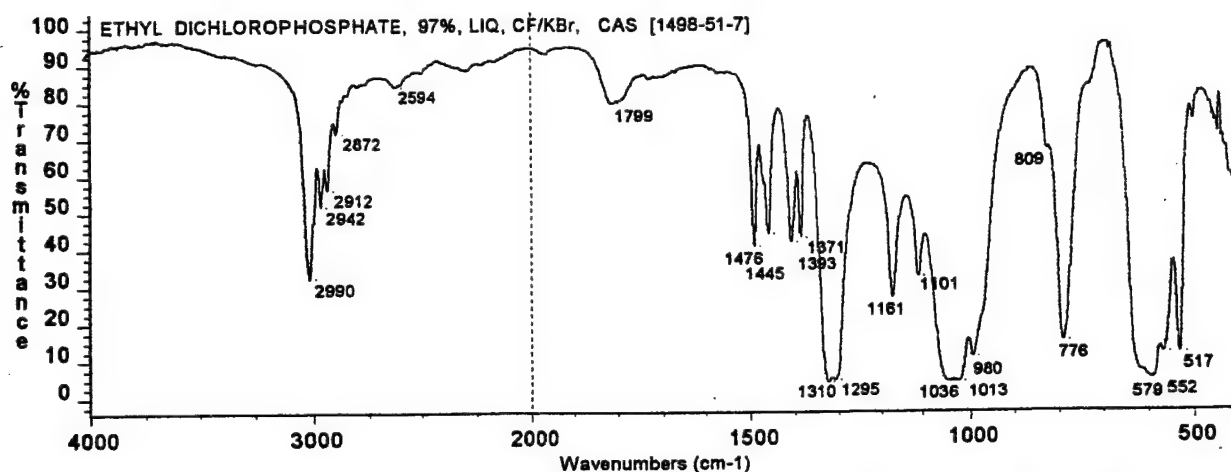
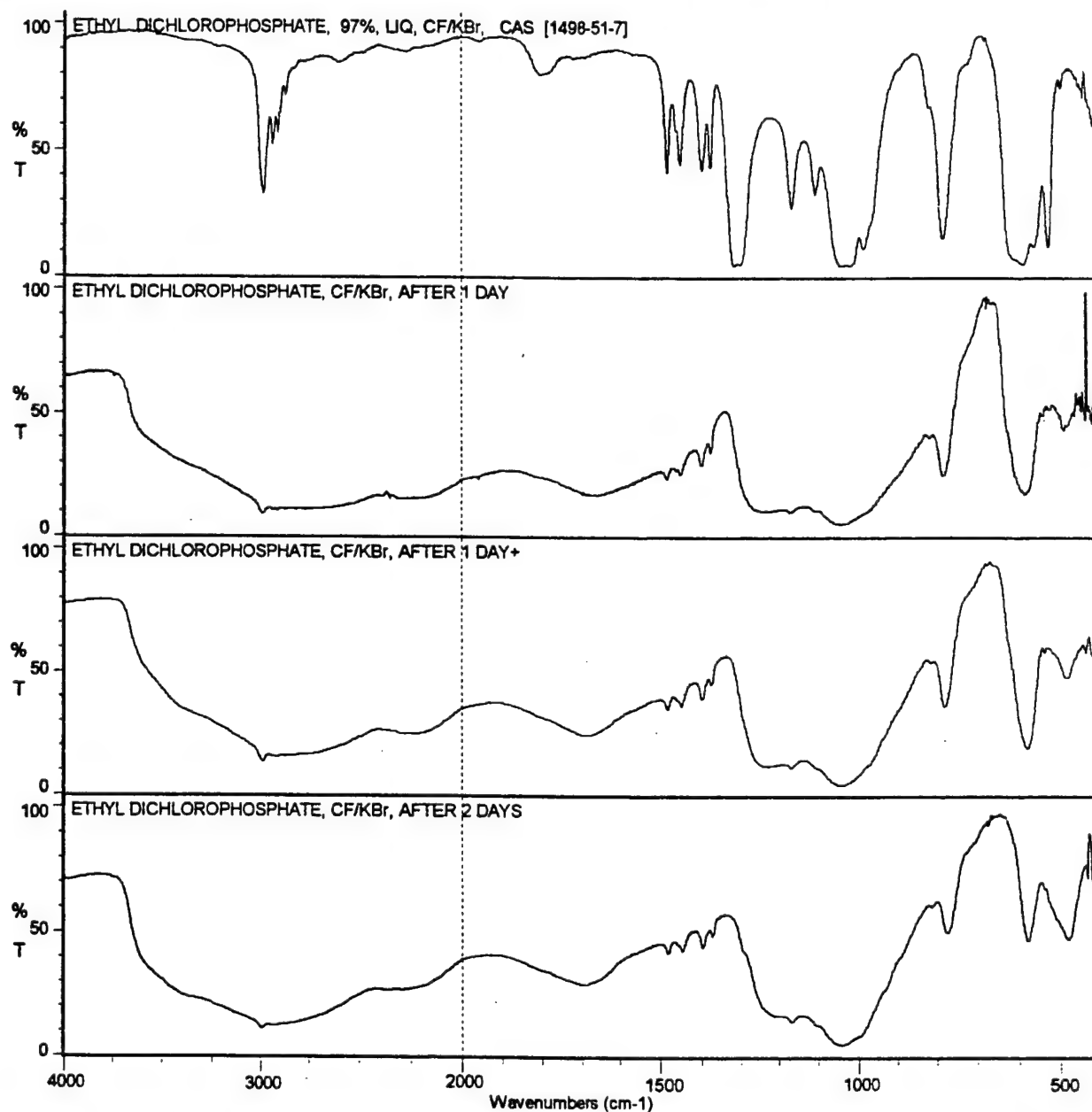


Figure 72 ETHYL PHOSPHORODICHLORIDATE (ETHYL DICHLOROPHOSPHATE), LIQUID, CF/KBr

The effect of atmospheric moisture on the infrared spectrum of ethyl phosphorodichloridate is given in *Figure 73*. The infrared spectrum after 1 day shows the presence of the POH group as indicated by the broad bands near 2770, 2280 and 1670  $\text{cm}^{-1}$ . Some PCl is probably still present as indicated by the band near 579  $\text{cm}^{-1}$ . The P=O stretching band has dropped from near 1300  $\text{cm}^{-1}$  to 1224  $\text{cm}^{-1}$ . The P-O-Ethyl group is still present as indicated by the bands at 2990, 1479, 1445, 1396, 1373, 1167, 1041 and 779  $\text{cm}^{-1}$ . By the second day of exposure to atmospheric moisture the spectrum shows a decrease in the P=O stretching frequency to 1205  $\text{cm}^{-1}$ . The POH and POethyl moieties are still present. The band

near  $578\text{ cm}^{-1}$  has greatly diminished in intensity and may now be due to the P-acid moiety and not to  $\text{PCl}$ . The resultant compound may now be represented as  $\text{H}_3\text{C}_2\text{-O-P=O(OH)}_2$ , ethyl phosphoric acid (ethyl dihydrogen phosphate). The compound may undergo further hydrolysis to form phosphoric acid,  $\text{HO-P=O(OH)}_2$ . The hydrolysis may be represented as follows:



**Figure 73 EFFECT OF ATMOSPHERIC MOISTURE ON ETHYL PHOSPHORODICHLORIDATE, (ETHYL DICHLOROPHOSPHATE), LIQUID, CF/KBr**



### 3.5 Impurities of Ethyl N,N-Dimethylphosphoramidocyanidate (GA, Tabun)

Triethyl phosphate (TEPO)

#### Triethyl Phosphate (TEPO)



The infrared spectrum of triethyl phosphate (TEPO) is reproduced as *Figure 74*. The band assignments are as follows: 3545  $\text{cm}^{-1}$  and 3489  $\text{cm}^{-1}$  vw ( $\text{H}_2\text{O}$ ), 2985  $\text{cm}^{-1}$  m ( $\nu_{\text{as}} \text{CH}_3$ ), 2935  $\text{cm}^{-1}$  w ( $\nu_{\text{as}} \text{CH}_2$ ), 2910  $\text{cm}^{-1}$  w ( $\nu_{\text{sy}} \text{CH}_3$ ), and 2873  $\text{cm}^{-1}$  vw ( $\nu_{\text{sy}} \text{CH}_2$ ), 1480  $\text{cm}^{-1}$  vw ( $\delta \text{OCH}_2$ ), 1445  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}} \text{CH}_3$ ), 1394  $\text{cm}^{-1}$  w ( $\omega \text{OCH}_2$ ), 1369  $\text{cm}^{-1}$  vw ( $\delta_{\text{sy}} \text{CH}_3$ ), 1275  $\text{cm}^{-1}$  ms and 1264  $\text{cm}^{-1}$  sh ( $\nu \text{P}=\text{O}$ ), 1167  $\text{cm}^{-1}$  and 1100  $\text{cm}^{-1}$  w ( $\text{CH}_3$  rock, characteristic of POEthyl), 1031  $\text{cm}^{-1}$  s ( $\nu \text{P}-\text{O}-\text{C}$ ), 976  $\text{cm}^{-1}$  ms ( $\nu \text{C}-\text{C}$  of POEthyl), 823 and 800  $\text{cm}^{-1}$  w and 744  $\text{cm}^{-1}$  (POC), 542 and 523  $\text{cm}^{-1}$  vw ( $\text{P}=\text{O}$  deformation).

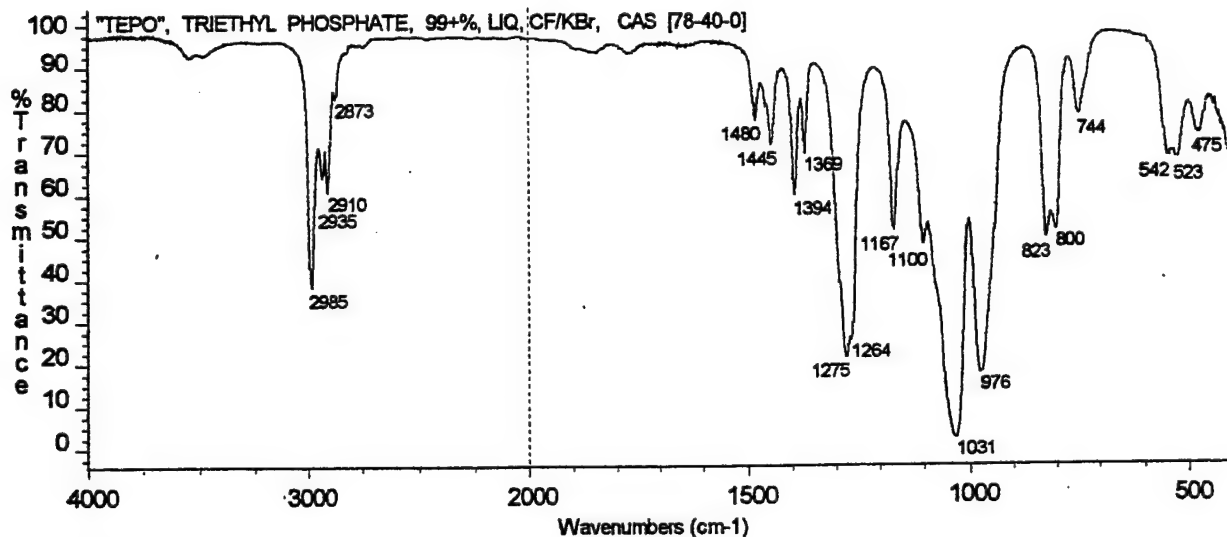
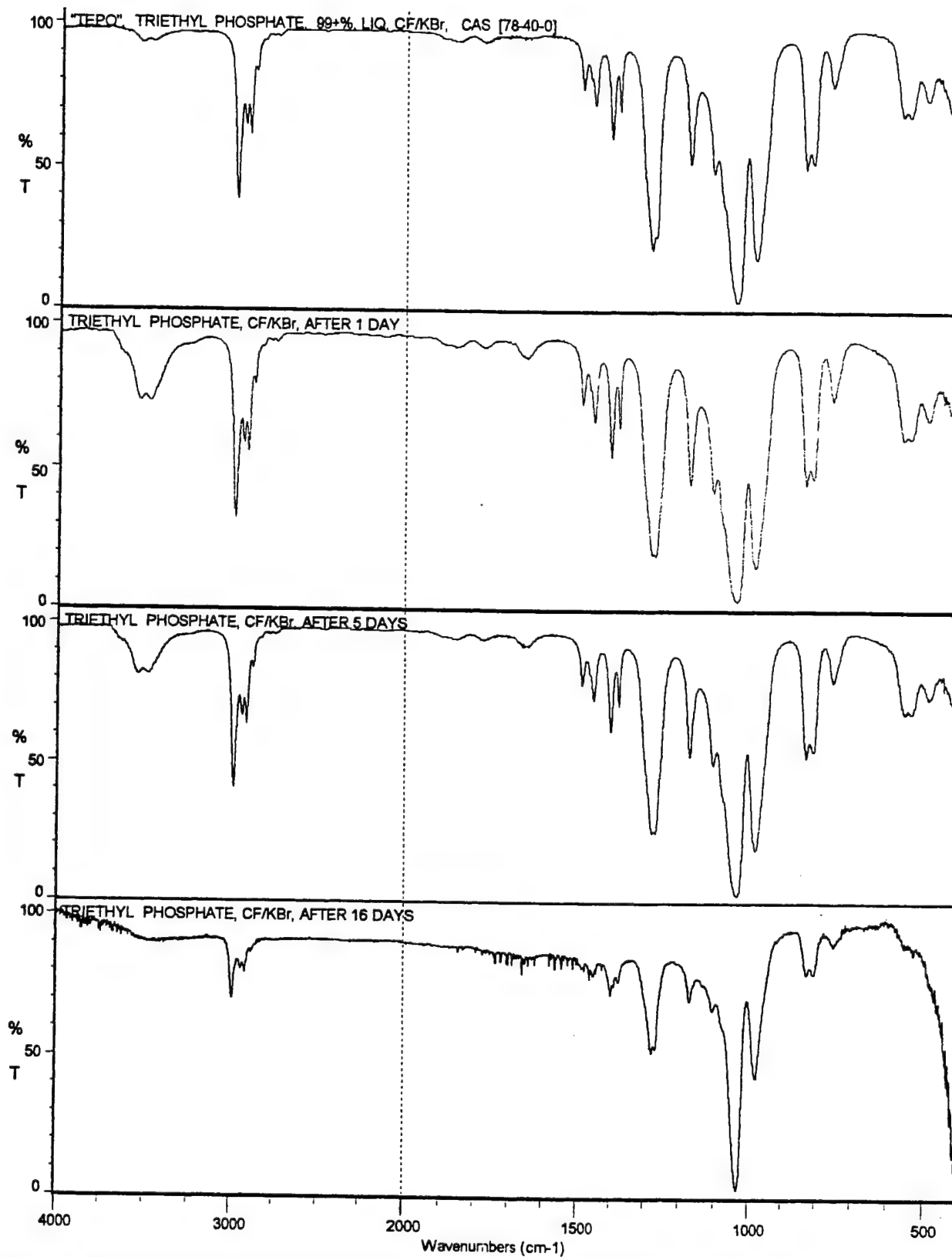


Figure 74 TRIETHYL PHOSPHATE (TEPO), 99+%, LIQUID, CF/KBr

The only atmospheric effect on triethyl phosphate was a slight pick-up of water by the compound on standing. This is shown in *Figure 75* by the increase in intensity of the water bands near 3500  $\text{cm}^{-1}$  with time. Also, at the 16 day period a lot of the compound has apparently evaporated as indicated by the relative intensities of the bands. Ordinate scale expansion was used to produce a full scale spectrum. This is indicated by the more than usual amount of noise in the spectrum.



**Figure 75** EFFECT OF ATMOSPHERIC MOISTURE ON TRIETHYL PHOSPHATE (TEPO), 99+%, LIQUID, CF/KBr

### 3.6 Decomposition Products of Ethyl N,N-Dimethylphosphoramidocyanidate (GA, Tabun)

Hydroxylamine hydrochloride

Phosphoric acid

Ethyl alcohol (Ethanol)

*sym*-Bis(dimethylamido)-diethyl pyrophosphate (GA Pyro)

Ethyl N,N-dimethylamidophosphoric acid, sodium salt, (sodium salt of GA Acid)

#### 3.6.1 Hydroxylamine Hydrochloride $\text{HONH}_2 \cdot \text{HCl}$

The infrared spectrum of hydroxylamine hydrochloride is given in *Figure 76*. Band assignments are as follows: a series of bands between  $3200$  and  $2800 \text{ cm}^{-1}$  are due to the  $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{NH}_3^+$  (the  $\nu$  O-H probably absorbs under these bands also), bands near  $2660 \text{ cm}^{-1}$  are combination bands enhanced by Fermi resonance;  $1567 \text{ cm}^{-1}$  m ( $\delta_{\text{as}}$   $\text{NH}_3^+$ ),  $1491 \text{ cm}^{-1}$  w ( $\delta_{\text{sy}}$   $\text{NH}_3^+$ ),  $1401 \text{ cm}^{-1}$  w ( $\beta$  OH ?),  $1189$  and  $1152 \text{ cm}^{-1}$  ms ( $\nu$  C-O),  $994 \text{ cm}^{-1}$  ms ( $\nu$  N-O),  $542 \text{ cm}^{-1}$  m ( $\text{NH}_3^+$  torsion ?).

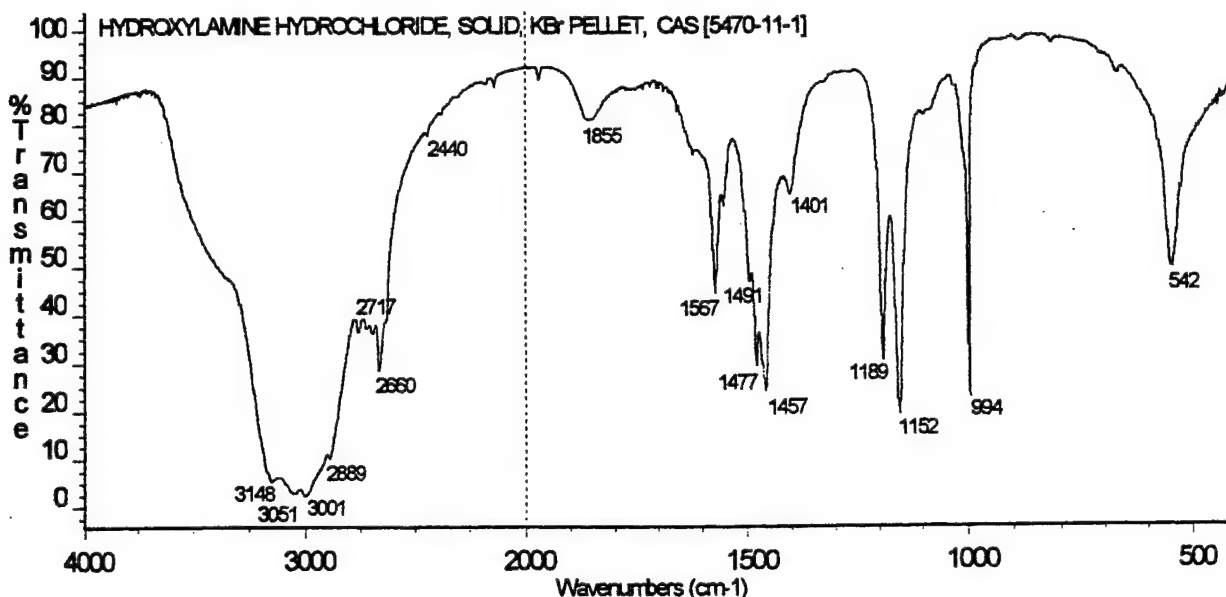


Figure 76 HYDROXYLAMINE HYDROCHLORIDE, SOLID, KBr PELLET

### 3.6.2 Phosphoric Acid $\text{H}_3\text{PO}_4$ , $(\text{OH})_3\text{P}=\text{O}$

The infrared spectrum of phosphoric acid is given in *Figure 77*. The band assignments are as follows:  $2883\text{ cm}^{-1}$ ,  $2342\text{ cm}^{-1}$ ,  $1654\text{ cm}^{-1}$  all m and broad (POH),  $1144\text{ cm}^{-1}$  ms ( $\nu\text{ P}=\text{O}$ ),  $1013\text{ cm}^{-1}$  s and  $889\text{ cm}^{-1}$  w ( $\nu\text{ P-OH}$ ),  $490\text{ cm}^{-1}$  m ( $\text{P}=\text{O}$  deformation).

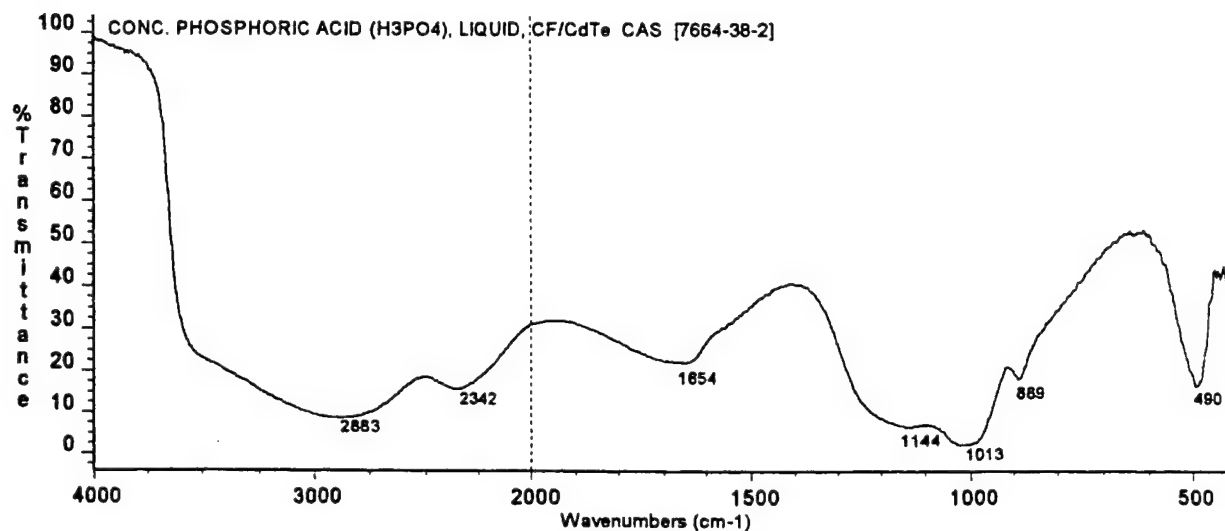
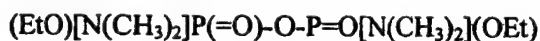


Figure 77 CONCENTRATED PHOSPHORIC ACID ( $\text{H}_3\text{PO}_4$ ), LIQUID, CF/CdTe

### 3.6.3 Ethyl Alcohol (Ethanol) $\text{CH}_3\text{-CH}_2\text{-OH}$

The infrared spectrum of ethyl alcohol (ethanol) is given in *Figure 78*. The band assignments are as follows:  $3357\text{ cm}^{-1}$  s ( $\nu\text{ OH}$  bonded),  $2975\text{ cm}^{-1}$  s,  $2928\text{ cm}^{-1}$  w and  $2892\text{ cm}^{-1}$  m ( $\nu\text{ CH}_3$  and  $\text{CH}_2$ ),  $1454\text{ cm}^{-1}$  w ( $\delta_{\text{as}}\text{ CH}_3$  and  $\delta\text{ CH}_2$ ),  $1420\text{ cm}^{-1}$  w ( $\beta\text{ OH}$ ),  $1381\text{ cm}^{-1}$  w ( $\delta_{\text{sy}}\text{ CH}_3$ ),  $1330\text{ cm}^{-1}$  w ( $\omega\text{ CH}_2$ ),  $1090$  and  $1050\text{ cm}^{-1}$  ms-s ( $\nu_{\text{o.o.p.}}\text{ C-C-O}$ ),  $881\text{ cm}^{-1}$  m ( $\nu_{\text{i.p.}}\text{ C-C-O}$ ),  $668\text{ cm}^{-1}$  w broad ( $\gamma\text{ C-OH}$ ).

### 3.6.4 sym-Bis(Dimethylamido)-diethyl Pyrophosphate (GA Pyro)



The infrared spectrum of GA Pyro, *sym*-bis(dimethylamido)-diethyl pyrophosphate, [bis(ethyl N,N-dimethylphosphoramidic) anhydride], was presented previously as *Figure 23* in section 3.1.9 under the discussion of GA. The effect of atmospheric moisture on GA Pyro was also discussed in section 3.1.9, *Figure 24*.

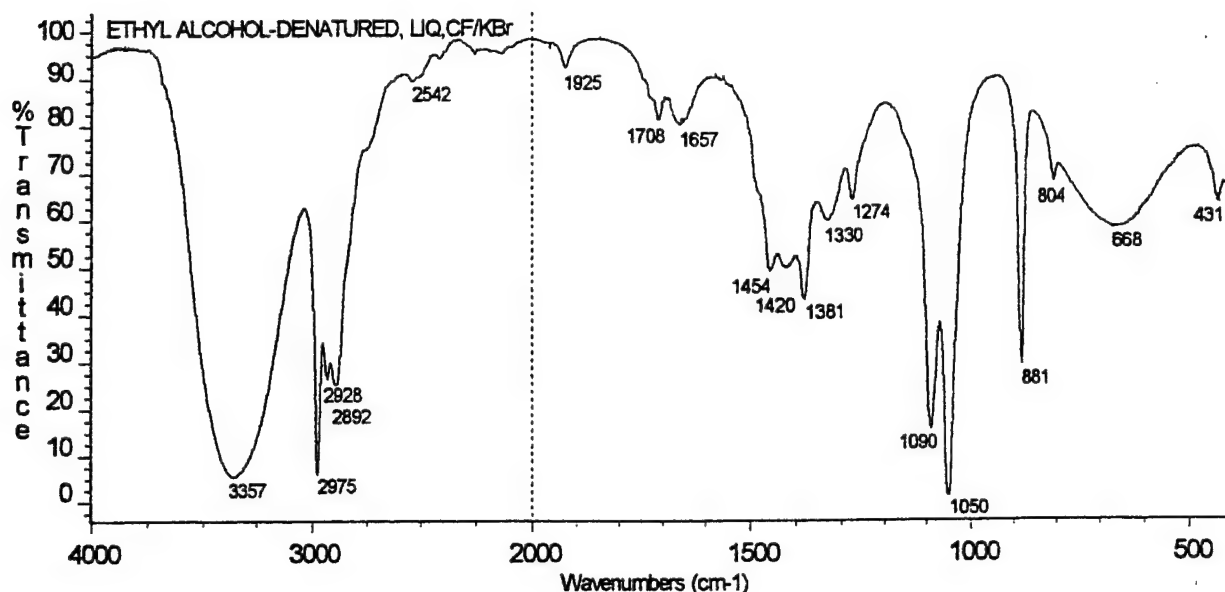
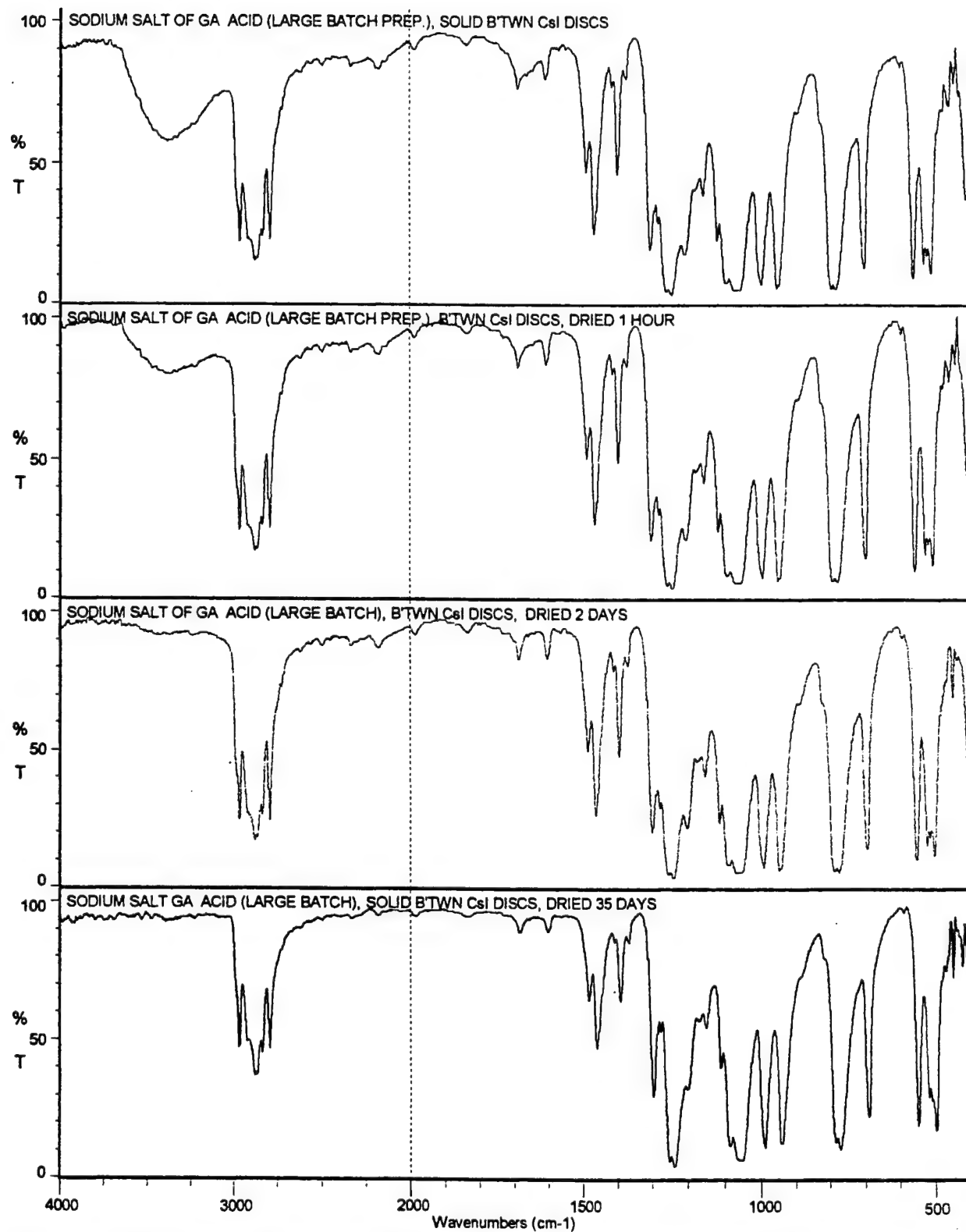


Figure 78 ETHYL ALCOHOL (DENATURED), LIQUID, CF/KBr

### 3.6.5 Ethyl N,N-Dimethylamidophosphoric Acid, Sodium Salt (Sodium Salt of GA Acid)



The infrared spectrum for the sodium salt of ethyl N,N-dimethylamidophosphoric acid (sodium salt of GA Acid), or the sodium salt of ethyl N,N-dimethylphosphoramidic acid, is given in *Figure 79*. This compound results from the basic hydrolysis of GA (Tabun). The band assignments (for the dried sample) are as follows: 2971  $\text{cm}^{-1}$  m, 2925  $\text{cm}^{-1}$  sh, 2882  $\text{cm}^{-1}$  and 2868  $\text{cm}^{-1}$  m, 2837  $\text{cm}^{-1}$  sh, 2794  $\text{cm}^{-1}$  m ( $\nu$   $\text{CH}_3$  and  $\nu$   $\text{CH}_2$ ), 1481  $\text{cm}^{-1}$  w ( $\delta$   $\text{OCH}_2$ ), 1458 m ( $\delta$   $\text{CH}_3$ ), 1390  $\text{cm}^{-1}$  w ( $\omega$   $\text{OCH}_2$ ), 1365  $\text{cm}^{-1}$  vw ( $\delta_{\text{sy}}$   $\text{CH}_3$ ), 1296  $\text{cm}^{-1}$  ms [ $\text{P}-\text{N}(\text{CH}_3)_2$ ], 1251  $\text{cm}^{-1}$  and 1237  $\text{cm}^{-1}$  s ( $\nu_{\text{as}}$   $\text{PO}_2^-$ ), 1200  $\text{cm}^{-1}$  sh and 1110  $\text{cm}^{-1}$  (?) w [ $\text{PN}(\text{CH}_3)_2$ ], 1087  $\text{cm}^{-1}$  sh ( $\nu$   $\text{P}-\text{O}-\text{C}$  ?), 1053  $\text{cm}^{-1}$  s ( $\nu_{\text{sy}}$   $\text{PO}_2^-$ ), 989  $\text{cm}^{-1}$  ms ( $\nu_{\text{as}}$   $\text{P}-\text{N}-\text{C}$ ), 943  $\text{cm}^{-1}$  ms ( $\nu$   $\text{C}-\text{C}$  of  $\text{POEthyl}$ ), 783 and 770  $\text{cm}^{-1}$  ms ( $\text{POC}$ ), 690  $\text{cm}^{-1}$  ms ( $\nu_{\text{sy}}$   $\text{PNC}$ ), 546  $\text{cm}^{-1}$  ms, 526  $\text{cm}^{-1}$  sh and 497  $\text{cm}^{-1}$  ms ( $\text{PO}_2^-$  deformation).



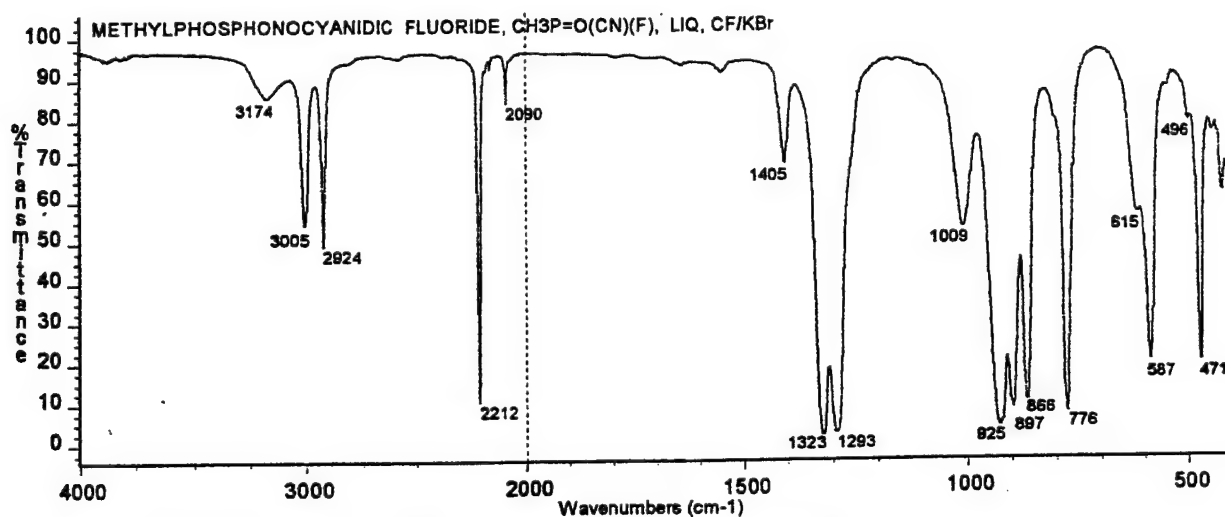
**Figure 79 INFRARED SPECTRUM OF THE SODIUM SALT OF ETHYL N,N-DIMETHYLAMIDOPHOSPHORIC ACID (SODIUM SALT OF GA ACID), SOLID BETWEEN Csl DISCS, AT VARYING DEGREES OF DRYNESS**

#### 4. ADDITIONAL COMPOUNDS OF INTEREST

##### 4.1 Methylphosphonocyanidic Fluoride

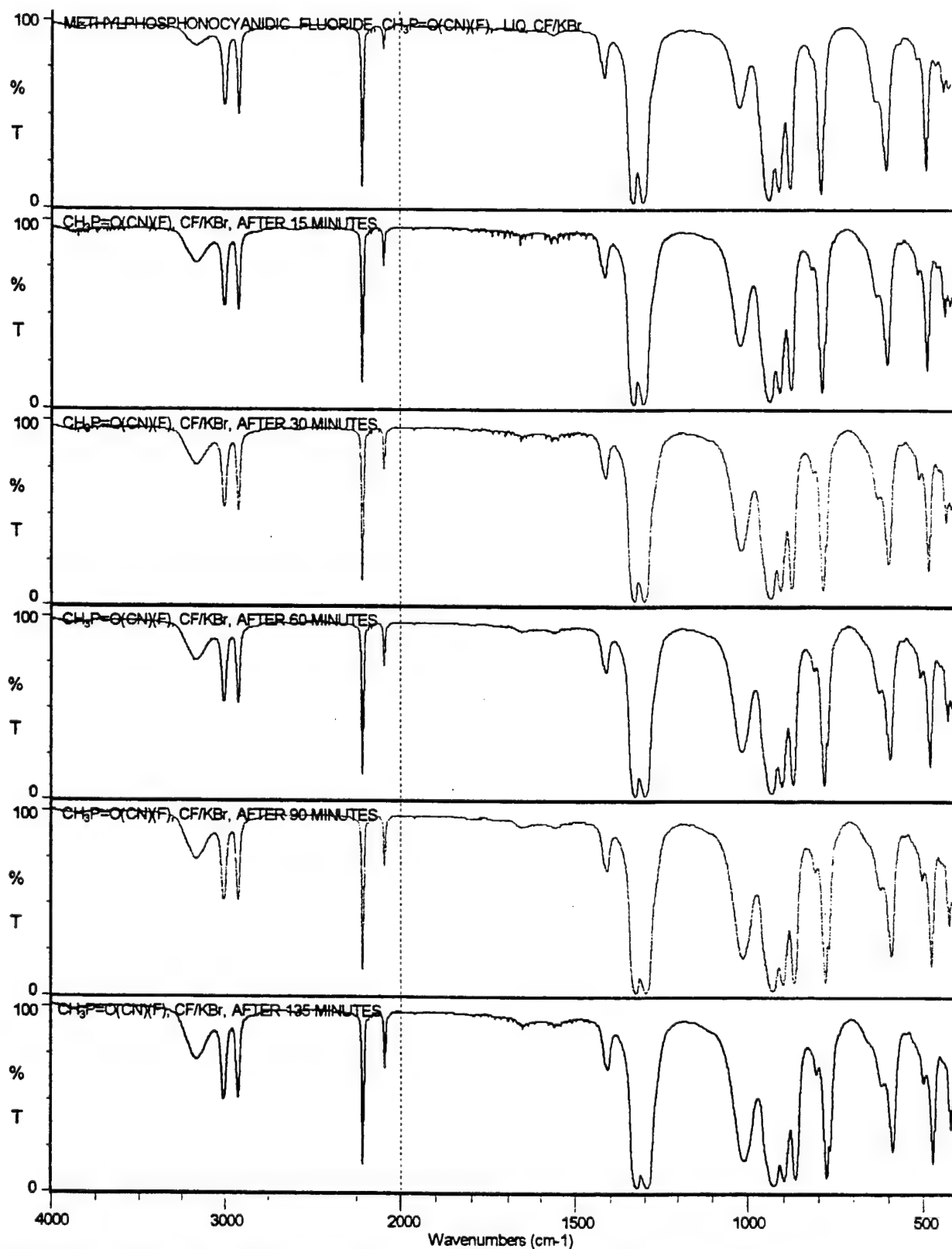


The infrared spectrum of methylphosphonocyanidic fluoride is reproduced as **Figure 80A**. The band assignments are as follows: ca 3174  $\text{cm}^{-1}$  vw ( $\nu$  C-H of HCN), 3005  $\text{cm}^{-1}$  w and 2924  $\text{cm}^{-1}$  w ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$ ), 2212  $\text{cm}^{-1}$  ms ( $\nu$   $\text{C}\equiv\text{N}$ ), 2090  $\text{cm}^{-1}$  vw ( $\nu$   $\text{C}\equiv\text{N}$  of HCN, hydrolysis product), 1405  $\text{cm}^{-1}$  w ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ), 1323  $\text{cm}^{-1}$  s ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ), 1293  $\text{cm}^{-1}$  s ( $\nu$  P=O), 1009  $\text{cm}^{-1}$  w ( $\nu$  P-OH ?, hydrolysis product), 925  $\text{cm}^{-1}$  s and 897  $\text{cm}^{-1}$  ms (P- $\text{CH}_3$  rock), 866  $\text{cm}^{-1}$  ms ( $\nu$  P-F), 776  $\text{cm}^{-1}$  s ( $\nu$  P-C), 587  $\text{cm}^{-1}$  ms (P-C $\equiv\text{N}$  ?), 471  $\text{cm}^{-1}$  ms ( $\delta$  P-F ?).



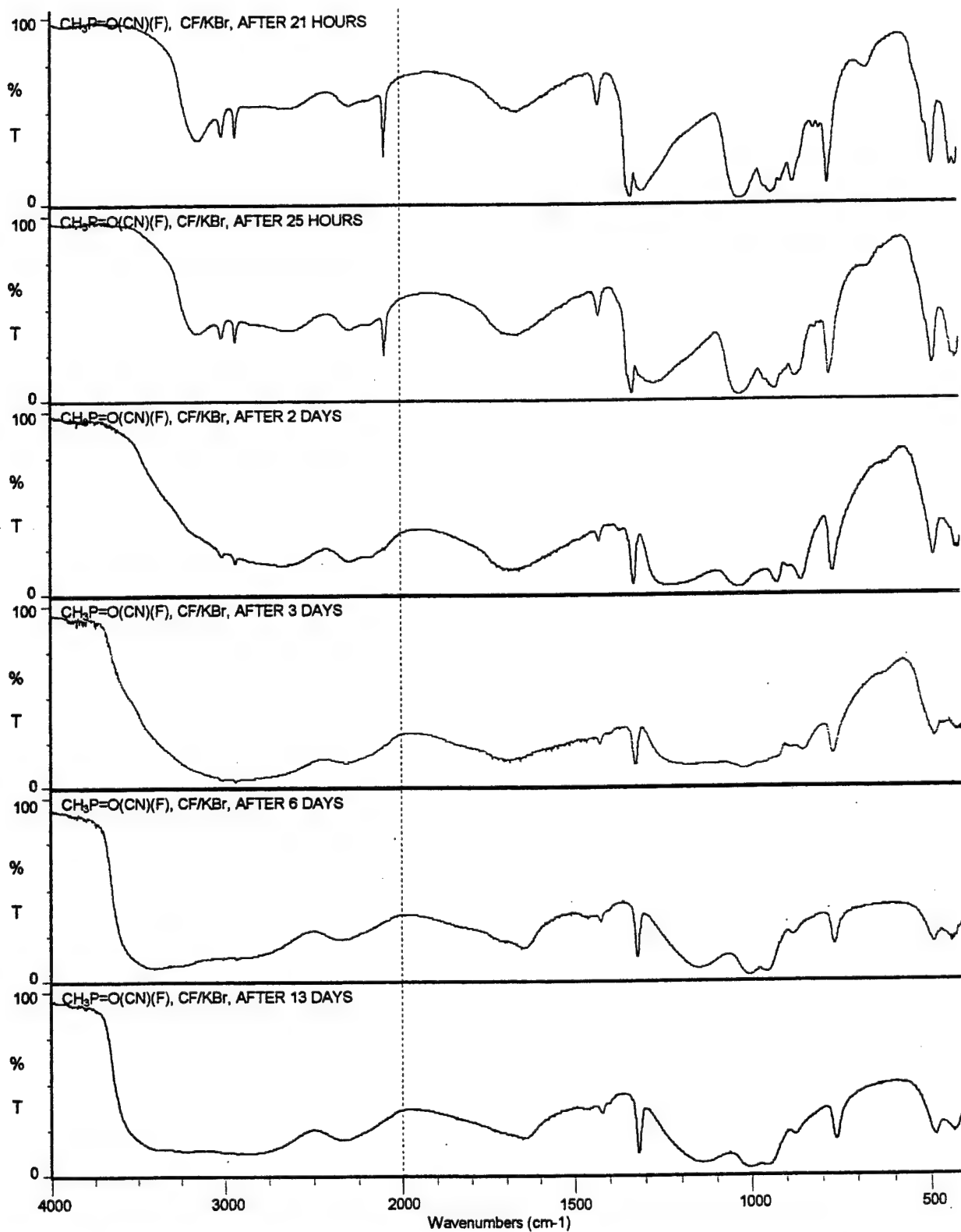
**Figure 80A METHYLPHOSPHONOCYANIDIC FLUORIDE, LIQUID, CF/KBr**

The exposure of methylphosphonocyanidic fluoride to atmospheric moisture is depicted by **Figure 80B**. As time passes to the 135 minute mark, bands at 3174 and 2090  $\text{cm}^{-1}$  (H-C $\equiv\text{N}$ ) have increased in intensity. Also increasing is the band at 1009  $\text{cm}^{-1}$  (P-OH). After 21 hours of exposure to atmospheric moisture, the  $\nu$   $\text{C}\equiv\text{N}$  band from the compound (2212  $\text{cm}^{-1}$ ) has disappeared from the spectrum, having been replaced by the  $\nu$   $\text{C}\equiv\text{N}$  of HCN (2090  $\text{cm}^{-1}$ ). Other bands now visible in the spectrum are: 3012 and 2935 vw, 1416 vw, 1325 s and 900  $\text{cm}^{-1}$  sh all due to the P- $\text{CH}_3$  group; ca 2634 and 2287 vw, 1653 w, 1017 s  $\text{cm}^{-1}$  due to P-OH; 867  $\text{cm}^{-1}$  ms ( $\nu$  P-F); 1298  $\text{cm}^{-1}$  ( $\nu$  P=O) a strong band but tailing off into broadness-indicating the possibility of more than one P=O containing species. The



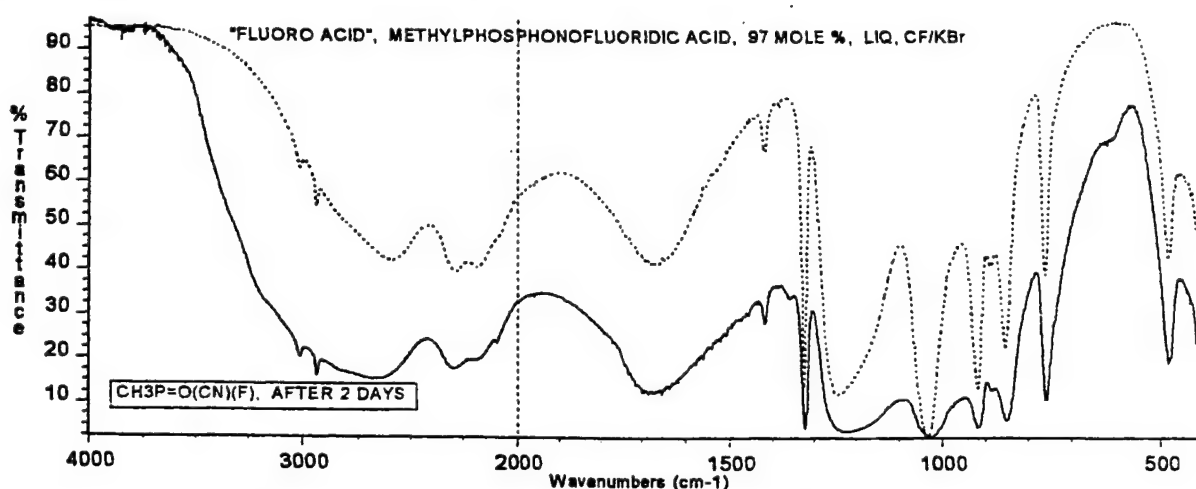
**Figure 80B METHYLPHOSPHONOCYANIDIC FLUORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE**





**Figure 80B METHYLPHOSPHONOCYANIDIC FLUORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)**

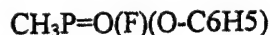
high value of this band could indicate the presence of a pyro compound, especially considering that there is a band near  $950\text{ cm}^{-1}$  ( $\nu\text{ P-O-P}$ ) and  $650\text{ cm}^{-1}$  which could also corroborate the existence of a pyro group. A compound such as methylphosphonofluoridic anhydride,  $\text{CH}_3(\text{F})\text{P}(=\text{O})\text{-O-P}(=\text{O})(\text{F})\text{CH}_3$ , would have a  $\nu\text{ P=O}$  (calculated value) of  $1302\text{ cm}^{-1}$ . Methylphosphonofluoridic acid (Fluoro Acid),  $\text{CH}_3\text{P=O}(\text{OH})(\text{F})$ , would absorb at  $1244\text{ cm}^{-1}$  and could contribute to the observed broadness of the  $\text{P=O}$  band. However, let us move to the sample after an exposure to atmospheric moisture of 2 days. Note that the POH bands near  $2678$ ,  $2294$ ,  $1650$  and  $1022\text{ cm}^{-1}$  are greatly enhanced from what they were previously. The band assigned to the  $\text{P=O}$  stretching region has decreased to  $1222\text{ cm}^{-1}$  and is still quite broad. *Figure 81* shows a comparison of the compound after 2 days to that of a known sample of Fluoro Acid. Note the excellent agreement between the two spectra despite the fact that the hydrolyzed sample is somewhat heavier in concentration than the Fluoro Acid.



**Figure 81** COMPARISON OF THE INFRARED SPECTRA OF FLURO ACID (UPPER IR) AND THE PRODUCT FROM METHYLPHOSPHONOCYANIDIC FLUORIDE AFTER AN EXPOSURE TO ATMOSPHERIC MOISTURE FOR 2 DAYS (LOWER IR)

The infrared spectrum continues to change, so that by the 6<sup>th</sup> through 13<sup>th</sup> days the sample has taken on the appearance of a wet methylphosphonic acid (MPA),  $\text{CH}_3\text{P=O}(\text{OH})_2$  (see *Figure 54* for the spectrum of a wet MPA). Thus, the hydrolysis of methylphosphonocyanidic fluoride may be summarized as follows:  $\text{CH}_3\text{P=O}(\text{CN})(\text{F}) - \text{HOH} \rightarrow (\text{F})\text{CH}_3\text{P}(=\text{O})\text{-O-P}(=\text{O})\text{CH}_3(\text{F}) [\text{?}] + \text{HCN} \uparrow$   
 $-\text{HOH} \rightarrow \text{CH}_3\text{P=O}(\text{OH})(\text{F}) - \text{HOH} \rightarrow \text{CH}_3\text{P=O}(\text{OH})_2 - \text{HF} \uparrow$ .

#### 4.2 Phenyl Methylphosphonofluoridate



The infrared spectrum of phenyl methylphosphonofluoridate is give in *Figure 82*. Band assignments are as follows: 3064  $\text{cm}^{-1}$  vw ( $\nu$  C-H aromatic), 3004  $\text{cm}^{-1}$  vw and 2930  $\text{cm}^{-1}$  w ( $\nu_{\text{as}}$  and  $\nu_{\text{sy}}$   $\text{CH}_3$ ), 1592  $\text{cm}^{-1}$  m, 1493  $\text{cm}^{-1}$  s and 1457  $\text{cm}^{-1}$  w (aromatic ring), 1415  $\text{cm}^{-1}$  vw ( $\delta_{\text{as}}$  P- $\text{CH}_3$ ), 1323  $\text{cm}^{-1}$  s ( $\delta_{\text{sy}}$  P- $\text{CH}_3$ ), 1292  $\text{cm}^{-1}$  s ( $\nu$  P=O), 1202  $\text{cm}^{-1}$  s ( $\nu$  C-O), 1166  $\text{cm}^{-1}$  m, 1072  $\text{cm}^{-1}$  w 1026  $\text{cm}^{-1}$  m and 1008  $\text{cm}^{-1}$  m ( $\beta$  C-H phenyl ring), 958  $\text{cm}^{-1}$  s ( $\nu$  P-O), 918 ms (P- $\text{CH}_3$  rock), 848  $\text{cm}^{-1}$  ms ( $\nu$  P-F), 763  $\text{cm}^{-1}$  m and 690  $\text{cm}^{-1}$  m (mono substituted aromatic ring), 721  $\text{cm}^{-1}$  w ( $\nu$  P-C ?).

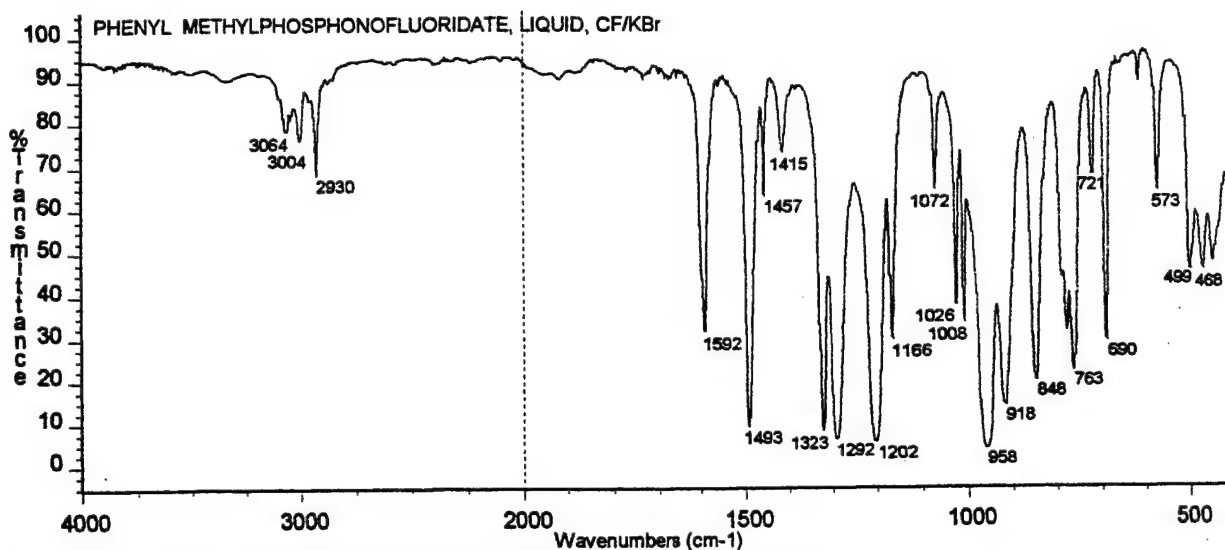
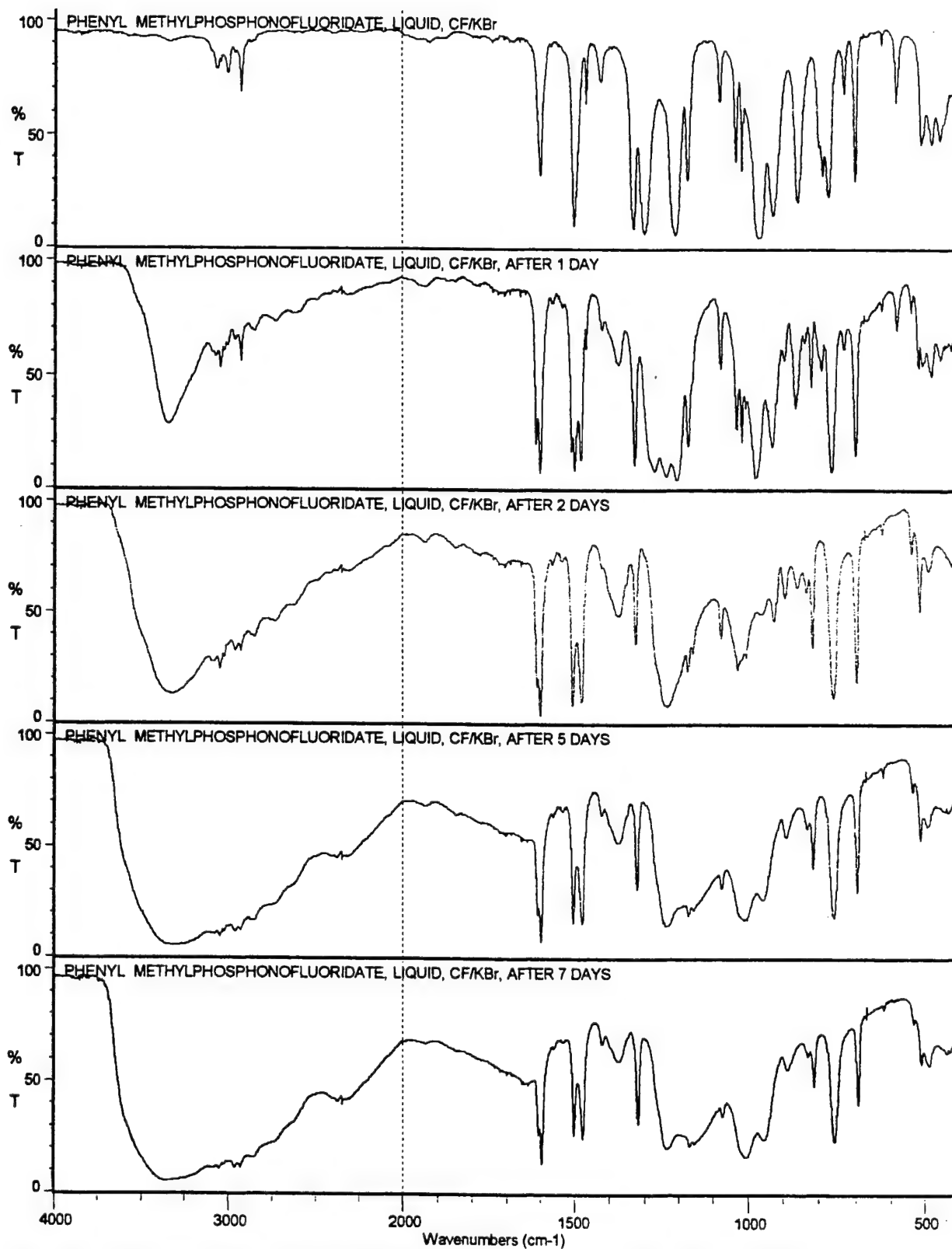
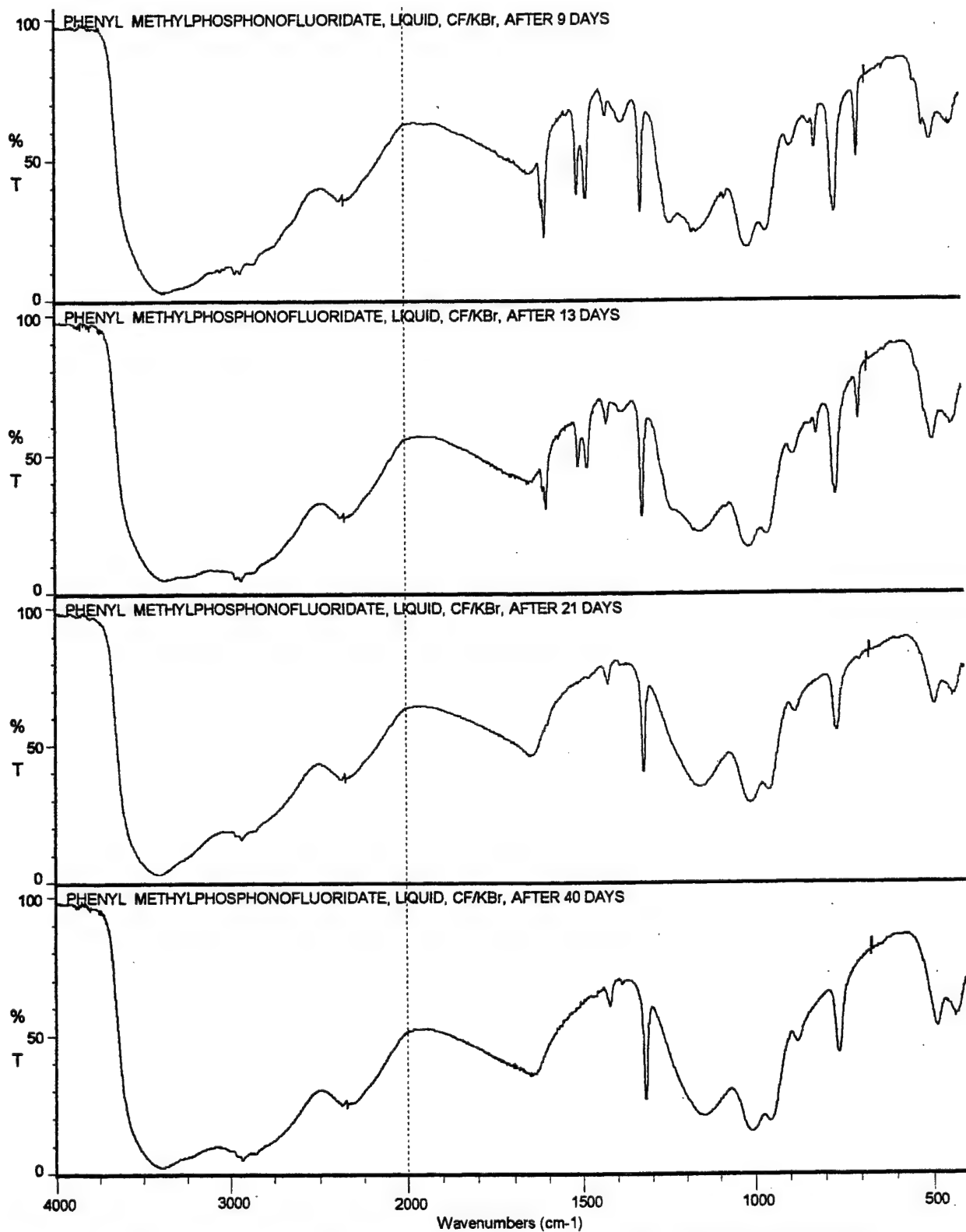


Figure 82 PHENYL METHYLPHOSPHONOFUORIDATE, LIQUID, CF/KBr

The effect of atmospheric moisture on phenyl methylphosphonofluoridate is shown by the infrared spectra reproduced in *Figure 83*. The infrared spectrum of the compound after 1 day of exposure to atmospheric moisture shows a strong band at 3348  $\text{cm}^{-1}$  due to bonded OH. New bands also appear at 1606  $\text{cm}^{-1}$ , 1501  $\text{cm}^{-1}$ , 1474  $\text{cm}^{-1}$ , 1367  $\text{cm}^{-1}$ , and 1229  $\text{cm}^{-1}$  and are believed to be due to the formation of phenol on hydrolysis. The P-F stretching band at 848  $\text{cm}^{-1}$  has decreased greatly in intensity. A new band also appears at 1263  $\text{cm}^{-1}$  which may be assigned to the P=O stretch from a pyro compound such as  $\text{CH}_3(\text{OC}_6\text{H}_5)\text{P}(=\text{O})-\text{O}-\text{P}(=\text{O})(\text{OC}_6\text{H}_5)\text{CH}_3$ , which would have a calculated P=O stretch

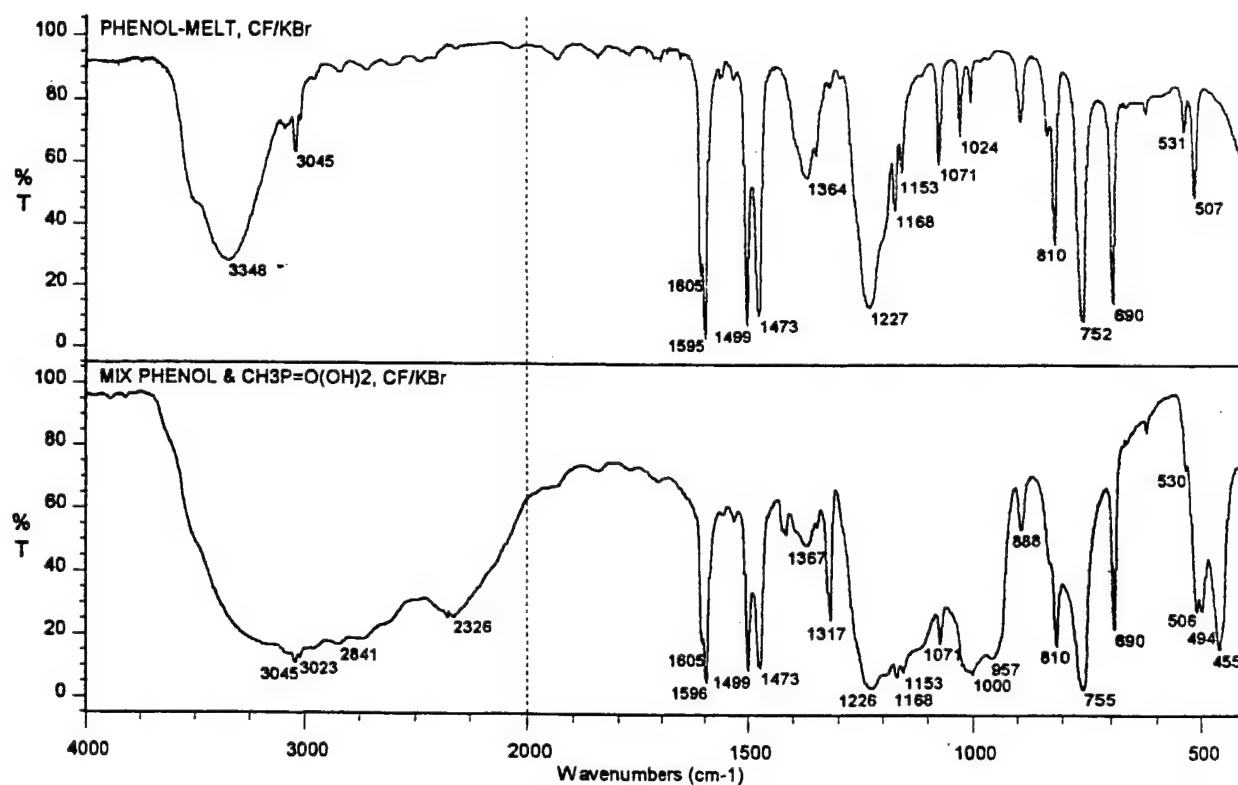


**Figure 83** PHENYL METHYLPHOSPHONOFUORIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE



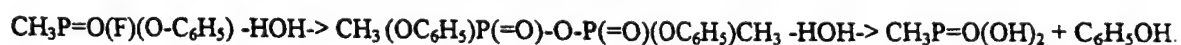
**Figure 83** PHENYL METHYLPHOSPHONOFUORIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

of  $1266\text{ cm}^{-1}$ . By day 2 only a single strong band is left in the range between  $1300\text{--}1200\text{ cm}^{-1}$  namely at  $1229\text{ cm}^{-1}$ . This may be assigned to a C-O stretch of phenol. A weak band near  $1368\text{ cm}^{-1}$  may be assigned to the OH deformation of phenol. The strong band that was at  $3348\text{ cm}^{-1}$  (after 1 day) has now broadened and moved to  $3323\text{ cm}^{-1}$  is assigned to the OH stretch of phenol (see *Figure 84 UPPER IR* for spectrum of phenol). As time progressed the infrared spectrum takes on the appearance of that for a mixture of phenol and methylphosphonic acid (see *Figure 84 LOWER IR* for the spectrum of a mix of phenol and methylphosphonic acid). By the 21<sup>st</sup> through 40<sup>th</sup> days the infrared spectrum becomes that of essentially a wet methylphosphonic acid,  $\text{CH}_3\text{P}=\text{O}(\text{OH})_2$ .



**Figure 84** *UPPER IR* PHENOL, MELTED BETWEEN KBr WINDOWS  
*LOWER IR* MIX OF PHENOL AND METHYLPHOSPHONIC ACID,  $\text{CH}_3\text{P}=\text{O}(\text{OH})_2$ , CF/KBr

Thus, the hydrolysis of phenyl methylphosphonofluoridate may be summarized as follows:

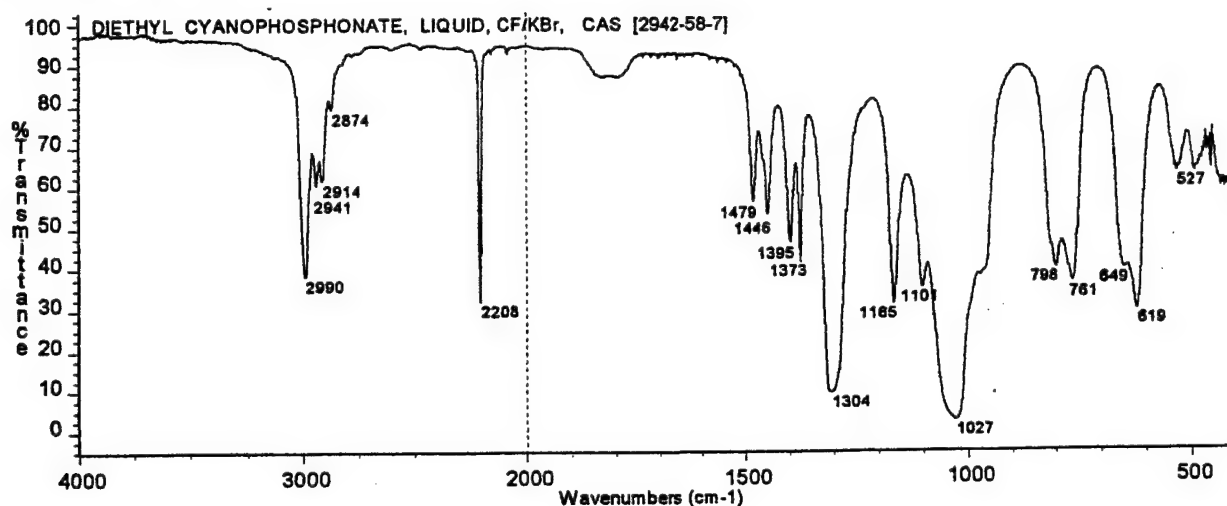


Some phenyl methylphosphonic acid,  $\text{CH}_3\text{P}=\text{O}(\text{OH})(\text{O}-\text{C}_6\text{H}_5)$ , may also have been formed.

### 4.3 Diethyl Cyanophosphonate

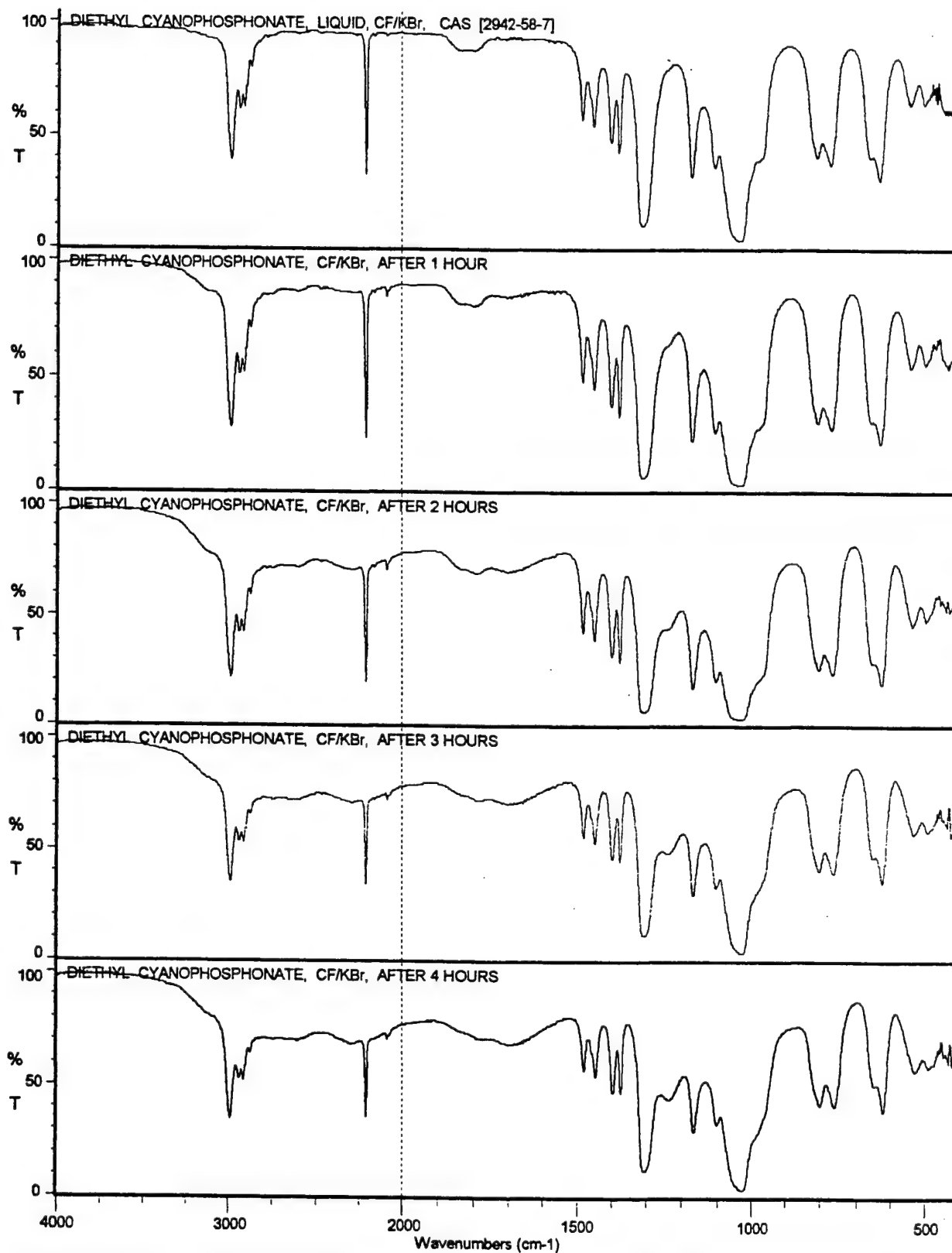


The infrared spectrum of diethyl cyanophosphonate is give in *Figure 85*. The band assignments are as follows:  $2990\text{ cm}^{-1}$  m ( $\nu_{\text{as}} \text{CH}_3$ ),  $2941\text{ cm}^{-1}$  w ( $\nu_{\text{as}} \text{CH}_2$ ),  $2914\text{ cm}^{-1}$  w ( $\nu_{\text{sy}} \text{CH}_3$ ),  $2874\text{ cm}^{-1}$  vw ( $\nu_{\text{sy}} \text{CH}_2$ ),  $2208\text{ cm}^{-1}$  m ( $\nu \text{C}\equiv\text{N}$ ),  $2084\text{ cm}^{-1}$  vvw ( $\nu \text{C}\equiv\text{N}$  of HCN),  $1830\text{ cm}^{-1}$  vw ( $1027 + 798 = 1825\text{ cm}^{-1}$ ),  $1792\text{ cm}^{-1}$  vw ( $1027 + 761 = 1788\text{ cm}^{-1}$ ),  $1479\text{ cm}^{-1}$  w ( $\delta \text{OCH}_2$ ),  $1446\text{ cm}^{-1}$  m ( $\delta_{\text{as}} \text{CH}_3$ ),  $1395\text{ cm}^{-1}$  m ( $\omega \text{OCH}_2$ ),  $1373\text{ cm}^{-1}$  m ( $\delta_{\text{sy}} \text{CH}_3$ ),  $1304\text{ cm}^{-1}$  ms ( $\nu \text{P}=\text{O}$ ),  $1165\text{ cm}^{-1}$  and  $1101\text{ cm}^{-1}$  w-m ( $\text{CH}_3$  rock, characteristic of POEt),  $1027\text{ cm}^{-1}$  s ( $\nu \text{P}-\text{O}-\text{C}$ ),  $971\text{ cm}^{-1}$  sh ( $\nu \text{C}-\text{C}$  of POEt),  $798\text{ cm}^{-1}$  m and  $761\text{ cm}^{-1}$  m (POC),  $619\text{ cm}^{-1}$  m ( $\nu \text{P}-\text{C}$  ?).



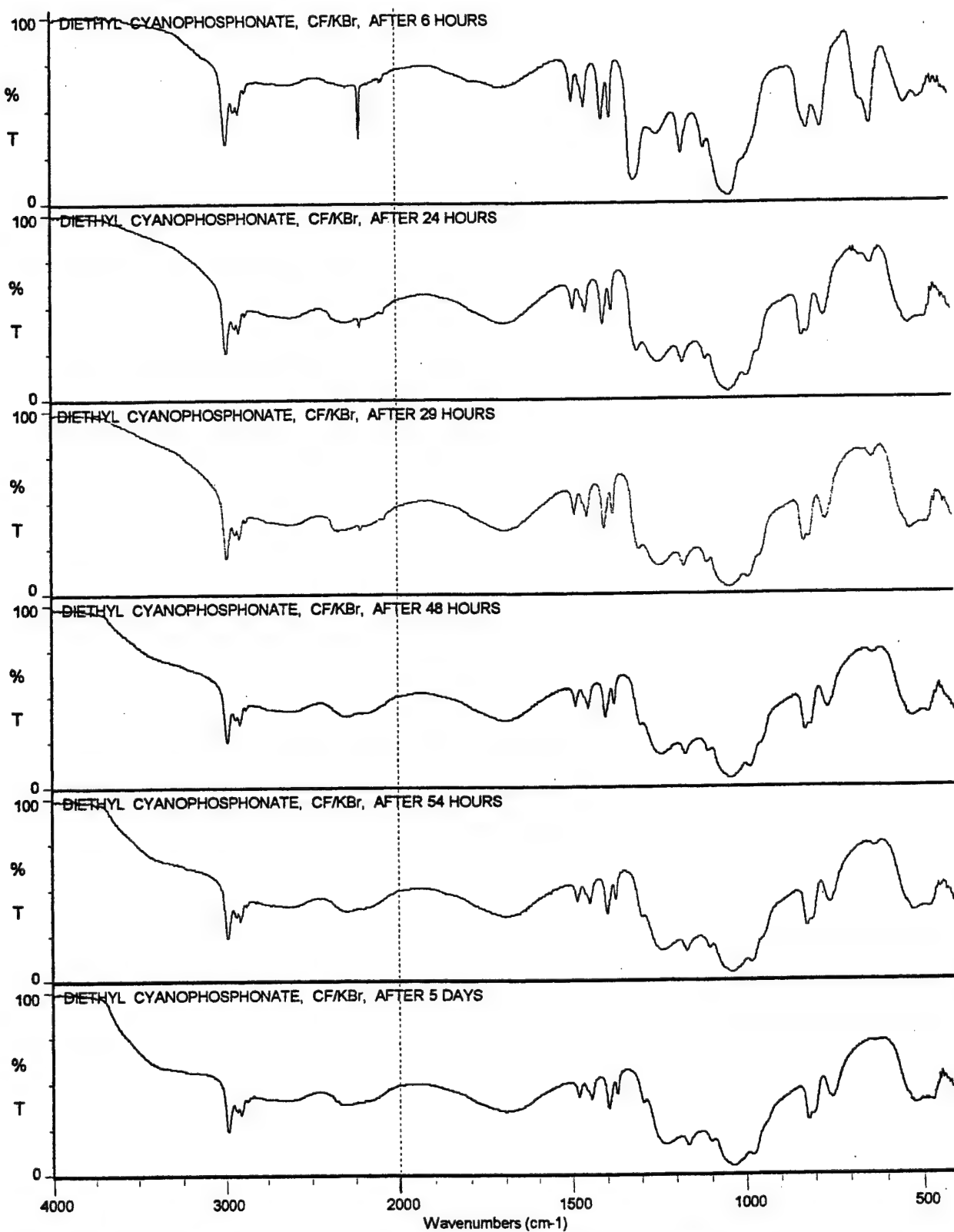
**Figure 85 DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr**

The effect of atmospheric moisture on diethyl cyanophosphonate is illustrated by the infrared spectra in *Figure 86*. After 1 hour exposure to atmospheric moisture the infrared spectrum for the compound shows a trace of HCN at ca  $2085$  and  $3115\text{ cm}^{-1}$ . After 2 hours the  $2208\text{ cm}^{-1}$  band ( $\nu \text{C}\equiv\text{N}$ ) shows a slight decrease in intensity with a corresponding small increase in the  $2085\text{ cm}^{-1}$  (HCN) band. Bands due to the POH moiety begin to appear in the spectrum near  $2600$  and  $1700\text{ cm}^{-1}$ , and a new band appears at  $1235\text{ cm}^{-1}$  which could be due to the  $\text{P}=\text{O}$  stretching of an P-acid moiety. The formation of a P-acid continues as the  $\text{C}\equiv\text{N}$  band at  $2208$  decreases in intensity with time. The  $\text{P}=\text{O}$  stretching band

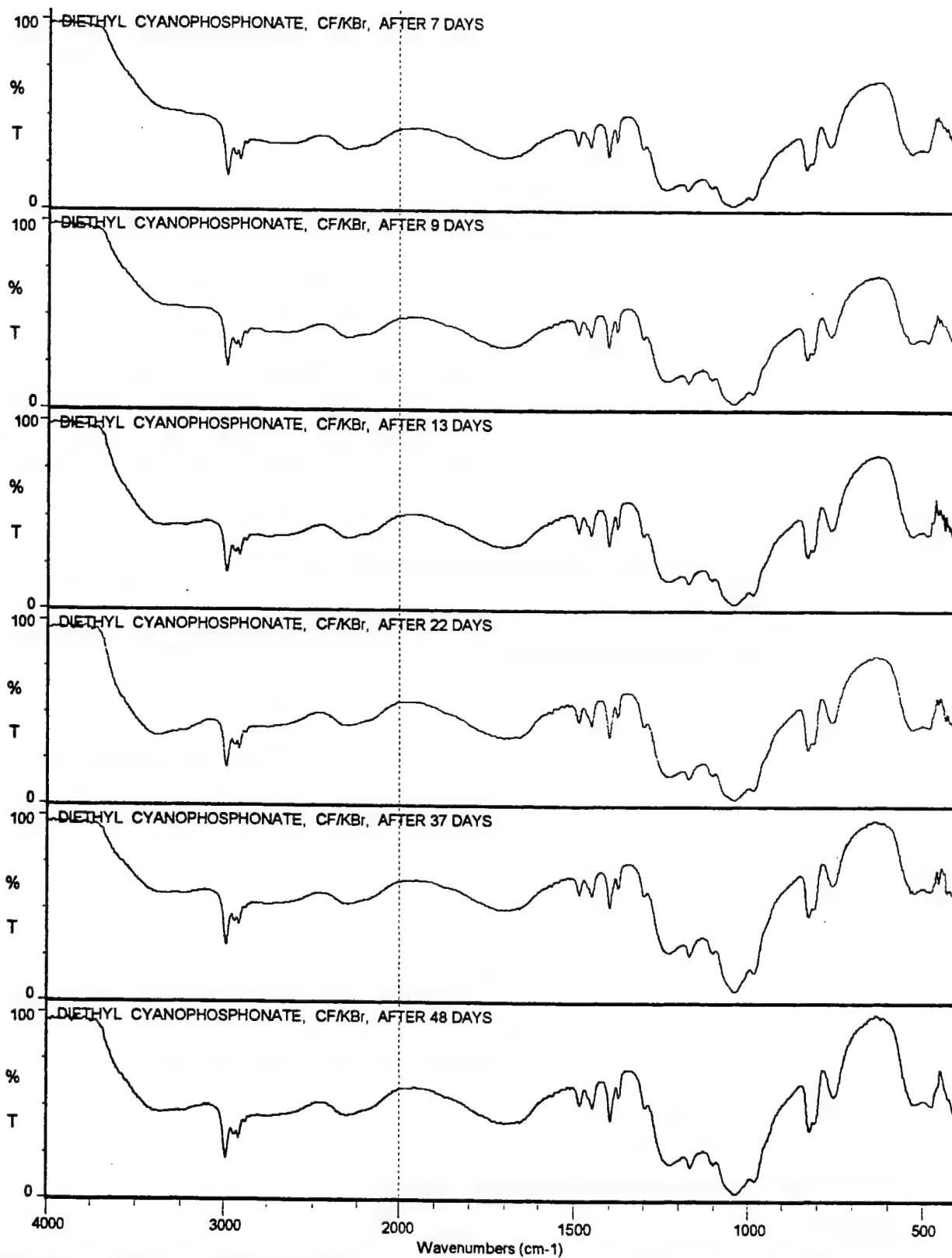


**Figure 86 DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE**





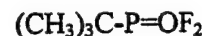
**Figure 86** DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)



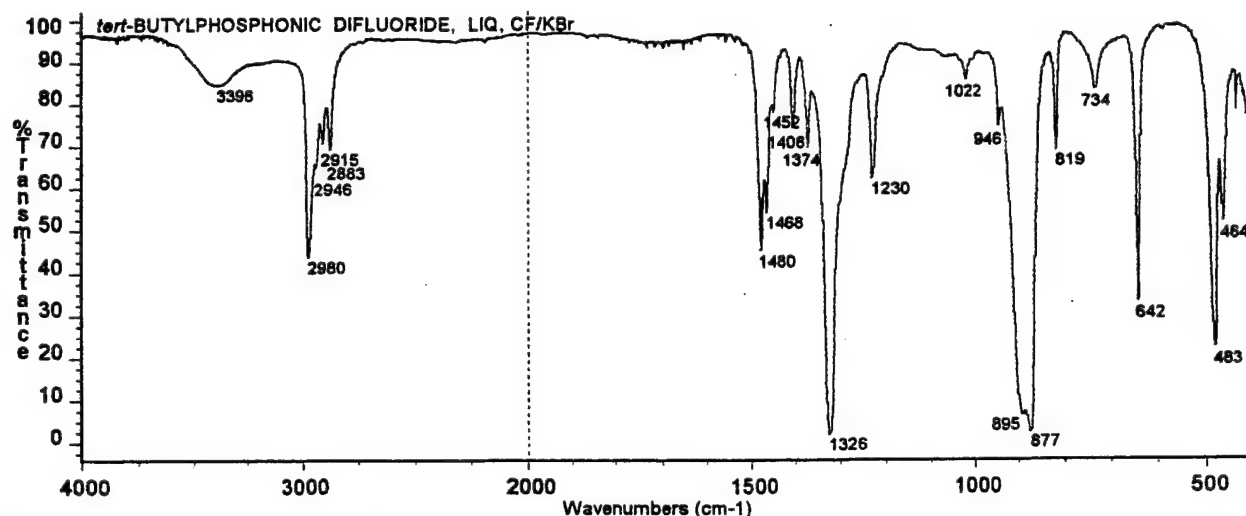
**Figure 86** DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

near  $1300\text{ cm}^{-1}$  also decreases in intensity as hydrolysis occurs. By 48 hours of exposure to atmospheric moisture the infrared spectrum of the sample corresponds to that of a P-acid, mostly likely, diethyl hydrogen phosphate  $[\text{HO}-\text{P}=\text{O}(\text{OEt})_2]$ . This result holds for the rest of the time of exposure that is, 48 days. Even after 48 days a weak band remains at  $1294\text{ cm}^{-1}$ , could this be due to the presence of a pyro compound, namely tetraethyl pyrophosphate (TEPP) or diethyl phosphoric anhydride,  $(\text{EtO})_2\text{P}(=\text{O})-\text{O}-\text{P}(=\text{O})(\text{OEt})_2$ ? The  $\text{P}=\text{O}$  stretch for this compound would occur near  $1290\text{ cm}^{-1}$ .

#### 4.4 *t*-Butylphosphonic Difluoride

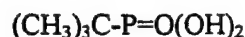


The infrared spectrum of *t*-butylphosphonic difluoride is given in **Figure 87**. The bands assignments are as follows:  $3396\text{ cm}^{-1}$  vw ( $\text{H}_2\text{O}$ ),  $2980\text{ cm}^{-1}$  m ( $\nu_{\text{as}}\text{ CH}_3$ ),  $2946\text{ cm}^{-1}$  sh ( $1480 + 1468 = 2948\text{ cm}^{-1}$ ),  $2915\text{ cm}^{-1}$  w,  $2883\text{ cm}^{-1}$  w ( $\nu_{\text{sy}}\text{ CH}_3$ ),  $1480\text{ cm}^{-1}$  m and  $1468\text{ cm}^{-1}$  w ( $\delta_{\text{as}}\text{ CH}_3$ ),  $1406\text{ cm}^{-1}$  w and  $1374\text{ cm}^{-1}$  w ( $\delta_{\text{sy}}\text{ CH}_3$ ),  $1326\text{ cm}^{-1}$  s ( $\nu\text{ P}=\text{O}$ ),  $1230\text{ cm}^{-1}$  w (*t*-butyl skeletal),  $946\text{ cm}^{-1}$  vw ( $\text{CH}_3$  rock),  $895\text{ cm}^{-1}$  sh and  $877\text{ cm}^{-1}$  s ( $\nu\text{ PF}_2$ ),  $642\text{ cm}^{-1}$  m ( $\nu\text{ P}-\text{C}$  ?),  $483\text{ cm}^{-1}$  ms and  $464\text{ cm}^{-1}$  w ( $\text{P}-\text{F}$  deformations ?).



**Figure 87** *t*-BUTYLPHOSPHONIC DIFLUORIDE, LIQUID, CF/KBr

#### 4.5 *t*-Butylphosphonic Acid



The infrared spectrum for *t*-butylphosphonic acid is given in **Figure 88**. The band assignments are as follows:  $2978\text{ cm}^{-1}$  w ( $\nu_{\text{as}}\text{ CH}_3$ ),  $2938\text{ cm}^{-1}$  vw ( $1470 \times 2 = 2940\text{ cm}^{-1}$  ?),  $2909\text{ cm}^{-1}$  vw,  $2875\text{ cm}^{-1}$

vw ( $\nu_{\text{sy}}$  CH<sub>3</sub>), 2754 cm<sup>-1</sup> m and 2311 cm<sup>-1</sup> m (POH), 1481 cm<sup>-1</sup> m and 1470 cm<sup>-1</sup> w ( $\delta$  CH<sub>3</sub>), 1397 cm<sup>-1</sup> w and 1370 cm<sup>-1</sup> w ( $\delta_{\text{sy}}$  CH<sub>3</sub>), 1243 cm<sup>-1</sup> m and 1217 cm<sup>-1</sup> m (*t*-butyl skeletal), 1192 cm<sup>-1</sup> ms ( $\nu$  P=O), 1005 cm<sup>-1</sup> s and 921 cm<sup>-1</sup> ( $\nu$  P-OH), 828 cm<sup>-1</sup> w (*t*-butyl CH<sub>3</sub> rock), 651 ms ( $\nu$  P-C), 502 and 486 cm<sup>-1</sup> ms (P=O deformation ?, *t*-butyl ?).

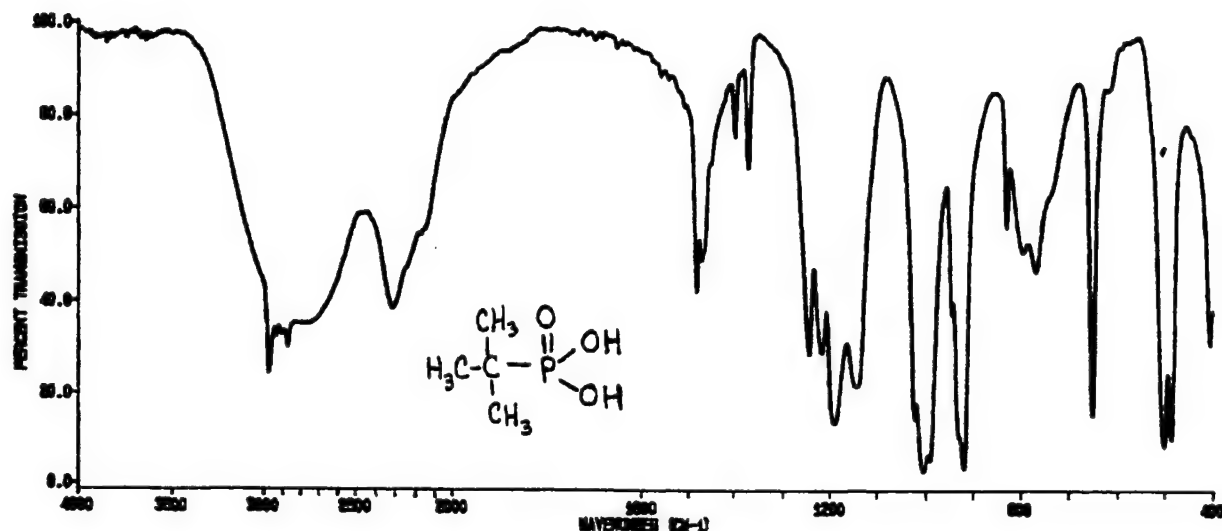
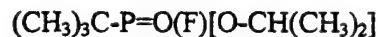


Figure 88 *t*-BUTYLPHOSPHONIC ACID, SOLID BETWEEN KBr DISCS

#### 4.6 Isopropyl *t*-Butylphosphonofluoridate



The infrared spectrum of isopropyl *t*-butylphosphonofluoridate is reproduced in *Figure 89*.

The band assignments are as follows: 2980 cm<sup>-1</sup> m ( $\nu_{\text{as}}$  CH<sub>3</sub>), 2939 cm<sup>-1</sup> w (1481 + 1465 = 2946 cm<sup>-1</sup> ?), 2877 cm<sup>-1</sup> vw ( $\nu_{\text{sy}}$  CH<sub>3</sub>), 1481 cm<sup>-1</sup> w and 1465 cm<sup>-1</sup> vw ( $\delta_{\text{as}}$  CH<sub>3</sub>), 1399 cm<sup>-1</sup> vw ( $\delta_{\text{sy}}$  CH<sub>3</sub> *t*-butyl), 1388 cm<sup>-1</sup> w and 1378 cm<sup>-1</sup> w ( $\delta_{\text{sy}}$  CH<sub>3</sub> isopropyl and *t*-butyl), 1354 cm<sup>-1</sup> vvw ( $\delta$  -CH isopropyl), 1283 cm<sup>-1</sup> ms ( $\nu$  P=O), 1228 cm<sup>-1</sup> w (*t*-butyl skeletal), 1180 cm<sup>-1</sup> vw and 1144 cm<sup>-1</sup> vw and 1105 cm<sup>-1</sup> w (a triplet of bands characteristic of P-O-isopropyl, involving C-C-C and C-C-O),<sup>c</sup> 1006 cm<sup>-1</sup> s ( $\nu$  P-O-C), 945 cm<sup>-1</sup> vw and 897 cm<sup>-1</sup> vw (CH<sub>3</sub> rock *t*-butyl and isopropyl), 849 cm<sup>-1</sup> ms ( $\nu$  P-F), 824 cm<sup>-1</sup> m (POC), 659 m ( $\nu$  P-C *t*-butyl), 520 cm<sup>-1</sup> w (P=O deformation ?), 487 cm<sup>-1</sup> vw (*t*-butyl ?).

<sup>c</sup> See general reference 4, page 346.

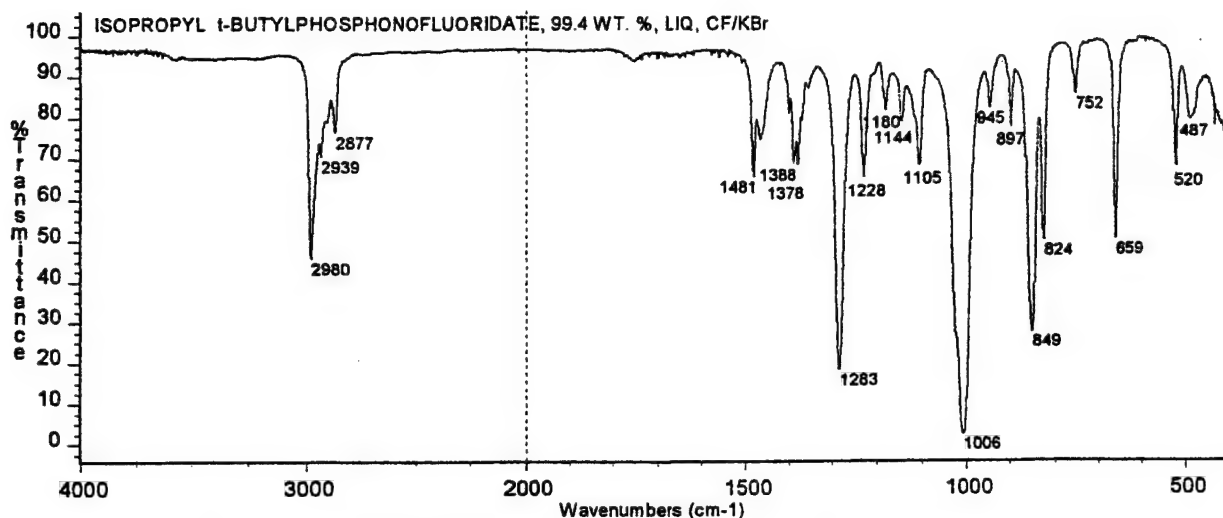


Figure 89 ISOPROPYL *t*-BUTYLPHOSPHONOFUORIDATE, 99.4 wt %, LIQUID, CF/KBr

#### 4.7 Isobutyl *t*-Butylphosphonofluoridate



The infrared spectrum of isobutyl *t*-butylphosphonofluoridate is given in *Figure 90*. Band assignments are as follows: 2969  $\text{cm}^{-1}$  ms ( $\nu_{\text{as}}$   $\text{CH}_3$ ), ca 2940  $\text{cm}^{-1}$  sh ( $\nu_{\text{as}}$   $\text{CH}_2$ ), 2912  $\text{cm}^{-1}$  vw ( $\nu$  -CH ?), 2877  $\text{cm}^{-1}$  m ( $\nu_{\text{sy}}$   $\text{CH}_3$  and  $\nu_{\text{sy}}$   $\text{CH}_2$ ), 1481  $\text{cm}^{-1}$  m and 1473  $\text{cm}^{-1}$  sh ( $\delta_{\text{as}}$   $\text{CH}_3$  and  $\delta$   $\text{CH}_2$ ), 1399  $\text{cm}^{-1}$  and 1370  $\text{cm}^{-1}$  w ( $\delta_{\text{sy}}$   $\text{CH}_3$ ), 1285  $\text{cm}^{-1}$  s ( $\nu$  P=O), 1229  $\text{cm}^{-1}$  m (*t*-butyl skeletal), 1182, 1167, 1130 and 1101  $\text{cm}^{-1}$  all vw (characteristic of isobutyl moiety ?), 1036  $\text{cm}^{-1}$  s ( $\nu$  P-O-C), 945  $\text{cm}^{-1}$  w ( $\nu$  C-C of isobutyl ?), 914  $\text{cm}^{-1}$  vw ( $\text{CH}_3$  rock ?), 847  $\text{cm}^{-1}$  ms ( $\nu$  P-F), 811  $\text{cm}^{-1}$  m (POC), 657  $\text{cm}^{-1}$  m (*t*-butyl moiety), 511  $\text{cm}^{-1}$  w (P=O deformation), 470  $\text{cm}^{-1}$  w (*t*-butyl moiety).

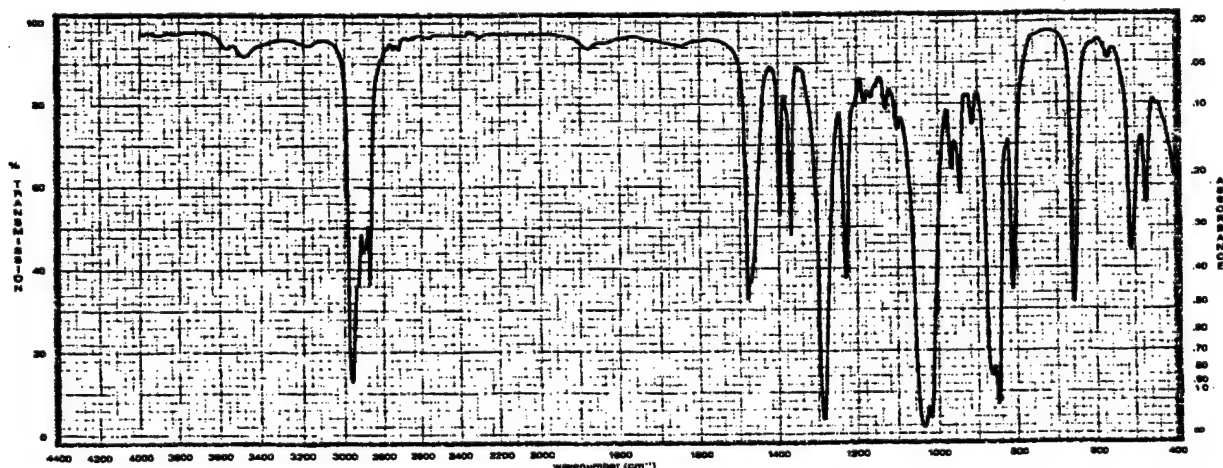
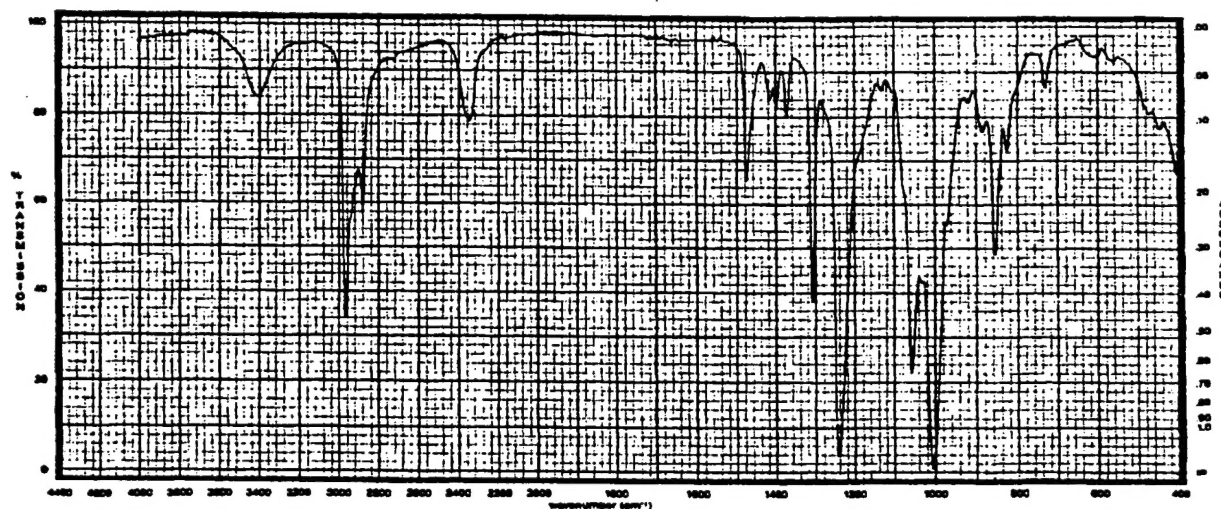


Figure 90 ISOBUTYL *t*-BUTYLPHOSPHONOFUORIDATE, LIQUID, CF/KBr

#### 4.8 Isobutyl Hydrogenmethylphosphinate

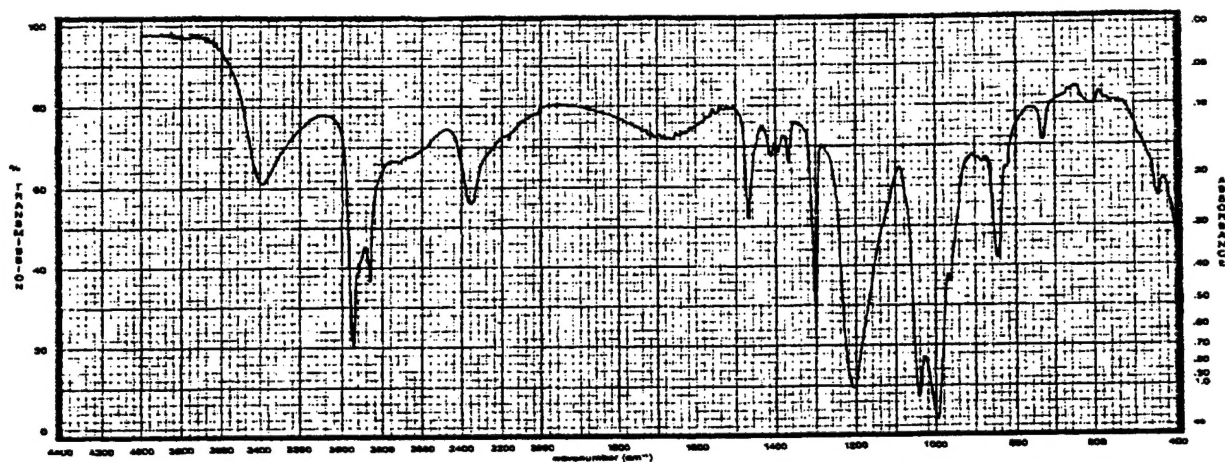


The infrared spectrum for isobutyl hydrogenmethylphosphinate is reproduced as *Figure 91*. The band assignments for the compound are as follows:  $3408\text{ cm}^{-1}$  vw ( $\text{H}_2\text{O}$ ),  $2962\text{ cm}^{-1}$  m ( $\nu_{\text{as}}\text{ CH}_3$ ),  $2877\text{ cm}^{-1}$  w ( $\nu_{\text{sy}}\text{ CH}_3$ ),  $2349\text{ cm}^{-1}$  vw ( $\nu\text{ P-H}$ ),  $1472\text{ cm}^{-1}$  w ( $\delta\text{ OCH}_2$  and  $\delta_{\text{as}}\text{ CH}_3$ ),  $1414\text{ cm}^{-1}$  vw ( $\delta_{\text{as}}\text{ P-CH}_3$ ),  $1397\text{ cm}^{-1}$  vw (partly  $\omega\text{ OCH}_2$  and  $\delta_{\text{sy}}\text{ CH}_3$  isopropyl),  $1369\text{ cm}^{-1}$  vw ( $\delta_{\text{sy}}\text{ CH}_3$  isopropyl),  $1302\text{ cm}^{-1}$  m ( $\delta_{\text{sy}}\text{ P-CH}_3$ ),  $1231\text{ cm}^{-1}$  s ( $\nu\text{ P=O}$ ),  $1048\text{ cm}^{-1}$  ms ( $\nu\text{ P-O-C}$ ),  $995\text{ cm}^{-1}$  s (P-H deformation),  $964\text{ cm}^{-1}$  sh ( $\nu\text{ C-C of O-isobutyl}$ ),  $883\text{ cm}^{-1}$  vvw ( $\text{CH}_3$  rock of isopropyl group),  $849\text{ cm}^{-1}$  m (P- $\text{CH}_3$  rock),  $822\text{ w}$  (POC),  $728\text{ cm}^{-1}$  vw ( $\nu\text{ P-C}$ ).

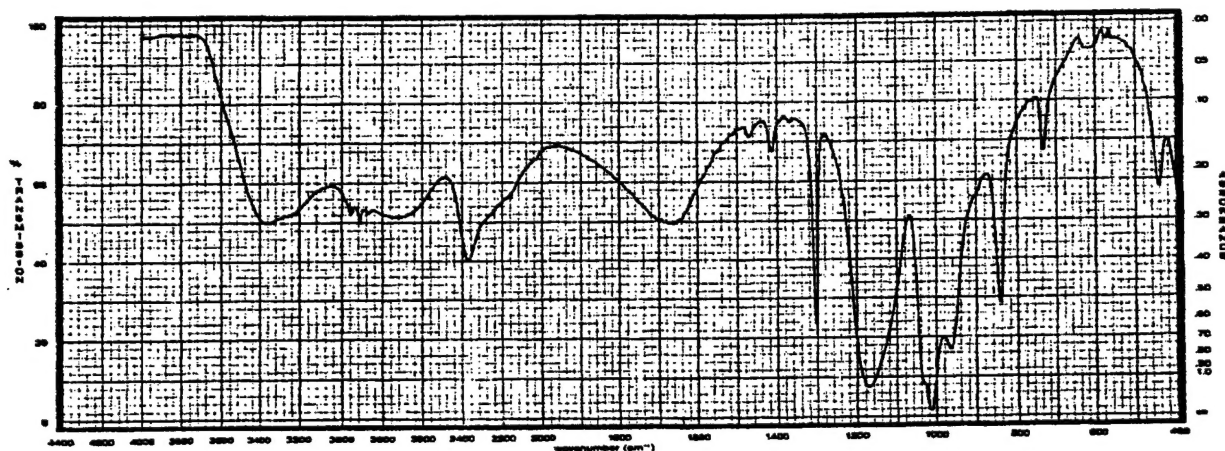


**Figure 91** ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID ,CF/KBr

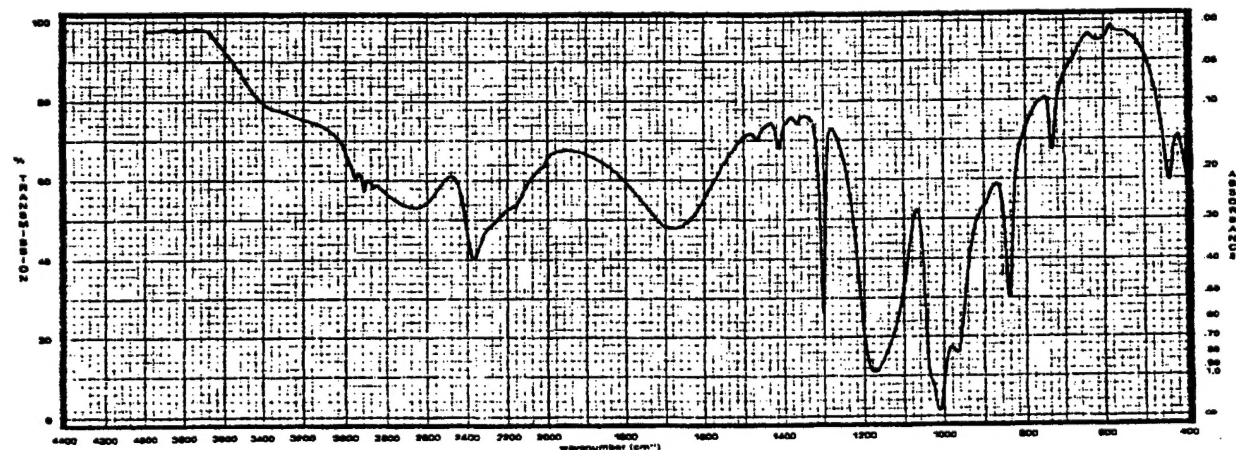
The infrared spectra representing the effect of atmospheric moisture on isobutyl hydrogenmethylphosphinate are given by *Figures 92A* through *92D*. After 24 hours of exposure to atmospheric moisture the infrared spectrum of the compound shows a broadened P=O stretching band now at  $1211\text{ cm}^{-1}$ . Some P-OH bands are evident near  $2700\text{ cm}^{-1}$  and under the P-H stretch at  $2369\text{ cm}^{-1}$  (indicated by a broadening of the band) and by a weak broad band near  $1680\text{ cm}^{-1}$ . After 12 days of exposure to atmospheric moisture the spectrum of the sample showed bands indicative of a P-acid. This observation also holds for the sample exposed to atmospheric moisture for 25 and 39 days. The hydrolysis product after 39 days (which appears to be the driest sample) has the following bands:  $2964\text{ cm}^{-1}$  vvw and  $2922\text{ vvw}$  ( $\nu_{\text{as}}$  and



**Figure 92A** ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/KBr, AFTER 24 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE



**Figure 92B** ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/KBr, AFTER 12 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE



**Figure 92C** ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/KBr, AFTER 25 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE



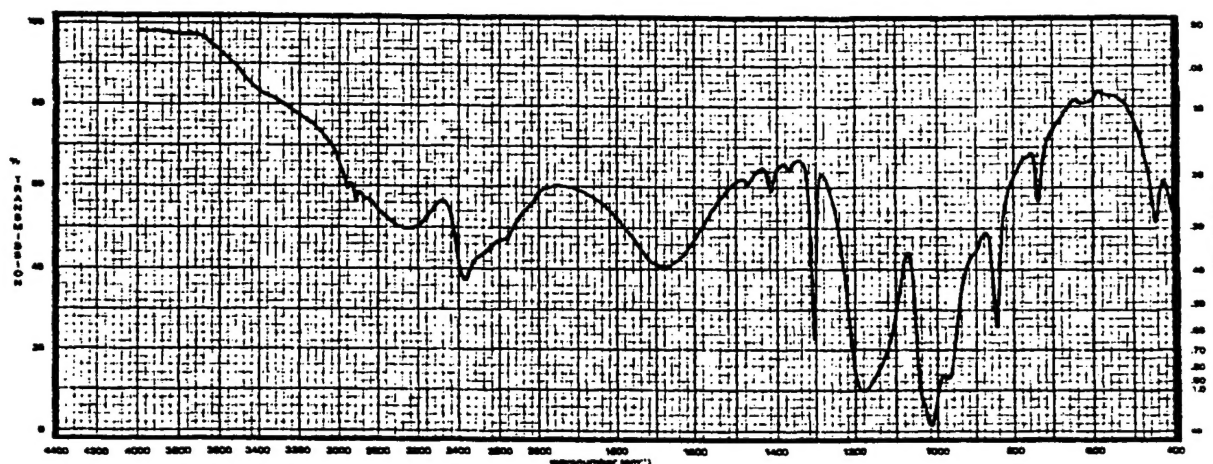
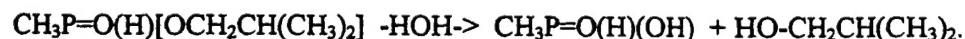


Figure 92D ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/KBr, AFTER 39 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

$\nu_{\text{sy}} \text{CH}_3$ ),  $2645 \text{ cm}^{-1}$  w broad (P-OH),  $2381 \text{ cm}^{-1}$  w ( $\nu$  P-H, this band is somewhat broad in shape and is also partly due to P-OH), ca  $1680 \text{ cm}^{-1}$  w broad (P-OH),  $1416 \text{ cm}^{-1}$  vvw ( $\delta_{\text{as}} \text{CH}_3$ ),  $1305 \text{ cm}^{-1}$  m ( $\delta_{\text{sy}} \text{P-CH}_3$ ),  $1180 \text{ cm}^{-1}$  ms broad ( $\nu \text{P=O}$ ),  $1017 \text{ cm}^{-1}$  s (P-H deformation),  $972 \text{ cm}^{-1}$  sh ( $\nu$  P-OH),  $844 \text{ cm}^{-1}$  m (P-CH<sub>3</sub> rock),  $736 \text{ cm}^{-1}$  w ( $\nu$  P-C),  $442 \text{ cm}^{-1}$  w (P=O deformation ?). The hydrolysis product appears to be methylphosphinic acid,  $\text{CH}_3\text{P=O(H)(OH)}$ . The hydrolysis may thus be summarized as follows:



## 5. CONCLUSIONS

The infrared spectra for a number of G-type compounds and well as precursors, impurities and decomposition products were presented and discussed. The effect of atmospheric moisture on the infrared spectra of these compounds was also examined and illustrated by spectra taken at various times of atmospheric exposure. It was shown, that when CsI windows were used to support the liquid films for spectral examination,  $\text{Cs}_2\text{SO}_4$  and  $\text{CsNO}_3$  (to a lesser degree) were also produced. The effect of grinding on some of the solid materials was also illustrated by representative infrared spectra.



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